ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

HETEROPHASE POLYMERIZATION OF PYRROLE AND ETOXYLATE NONYLPHENOL BY CERIUM (IV)

M.Sc. THESIS

Merve ÇAMOĞLU

Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PİROL'ÜN CERYUM (IV) ORTAMINDA ETOKSİ NONİLFENOL İLE HETEROFAZ POLİMERLEŞMESİ

YÜKSEK LİSANS TEZİ

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MAYIS 2014

Merve ÇAMOĞLU, a **M.Sc.** student of ITU **Institute of Science and Technology** 515111019, successfully defended the **thesis** entitled "**HETEROPHASE POLYMERIZATION OF PYRROLE AND ETOXYLATE NONYLPHENOL BY CERIUM (IV)**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 29 April 2014
Date of Defense : 28 May 2014

To my spouse and mother,

FOREWORD

I would like to thank all of the Assoc. Prof. Dr. Nesrin Köken, Prof. Dr. Nilgün Kızılcan for their advices and assistance during my Master's of Science study and the preparation of this thesis and generating the an enviroment in which it has been pleasure to work.

Finally, I also would like to thank my family and my friends who had been helped me when I needed help Esin Ateş also Barbaros Akkurt.

May 2014 Merve ÇAMOĞLU

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ABBREVIATIONS

CAN	**:** Cerium Ammonium Nitrate
ENP	**:** Nonlyphenol Etoxylated
FTIR	**:** Fourier Transform Infrared Spectroscopy
NP	**:** Nonlyphenol
PBT	**:** Persistent, Bioaccumulative and Toxic
Py	**:** Pyrrole
PPy	**:** Polypyrrole
PPV	**:** Polyphenylene vinylene
PSS	: Polystyrene sulphonate
SEM	**:** Scanning Electron Microscope

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HETEROPHASE POLYMERIZATION OF PYRROLE AND ETOXYLATE NONYLPHENOL BY CERIUM (IV)

SUMMARY

Polypyrrole (PPy) is one of the most investigated conducting polymers, due to its easy synthesis and good conductivity. Pyrrole with cerium (IV) ammonium salts show an improvement in solubility with respect to PPy. Redox systems of cerium (IV) ammonium salts and organic reducing agents are well known initiators for vinyl polymerization in aqueous media. Homopolymers, block copolymers and graft copolymers were obtained via cerium (IV) ammonium salts and reducing compounds such as alcohols, polyoils, acids, amines, thiols, thiourea and ketonic resins. Polystyrene, polyacrylonitrile and polyacrylic acid containing chain ends of ethoxylated nonyl phenol (ENP) were prepared using ceric-ethoxylated nonly phenol redox initiator system.

In this work, copolymers of pyrrole and ENP were synthesized via redox polymerization at room temperature. Different molar concentration is applied to the redox reaction of copolymer polypyrrole-nonlyphenol. The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions are minimized. This method has found wide applications in initiating various polymerization reactions and with industrial importance, low-temperature emulsion polymerizations Polymerization of pyrrole was performed by cerium (IV) ammonium nitrate in combination with ENP in acidic aqueous media. ENP served both as a reducing agent of the redox system and an emulsifier for pyrrole with poor solubility in water. ENP with changing number of ethoxy units (ENP 10 and ENP 30) were used in order to investigate the influence of ethoxylated component on the properties of the copolymers. The resulting copolymers were characterized with spectroscopic methods which is Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscope (SEM). The effect of the concentration of cerium salt and pyrrole on yield, solubility and conductivity was investigated as ENP type.

Results showed that yield of the copolymers strongly depend on Ce^{+4} concentrations while electrical conductivities of copolymers were measured to be 10^{-3} S/cm

PİROL'ÜN CERYUM (IV) ORTAMINDA ETOKSİ NONİLFENOL İLE HETEROFAZ POLİMERLEŞMESİ

ÖZET

Polimerler çok uzun yıllar yalıtkan özelliklerinden dolayı kullanılmıştır örnek olarak metal kablolara yalıtkan özellik kazanmak için plastik ile kaplanmışlardır. Iyonik polimerlerin elektiksel iletkenlik kazanması 1975 yılında olmuştur ve bundan sonra iyonik olarak iletken polimerler ve polimer elektrotlar geniş uygulama alanı bulmuştur. İletken polimerleri dört ana grup altında inceleyebilirz. Bunlar, konjuge iletken polimerler, yük transfer polimerler, iyonik iletken polimer ve iletken doldurulmuş polimerler. Konjuge iletken polimerler bu grupta en çok kullanılan iletken polimer tipidir. Konjuge yapısı polimerin yapısında bulunan sıralı tek ve çift bağlardan kaynaklanır ve p-orbitallerin devamlı olarak üstüste çakışması iletkenlik için gereklidir. Birçok organik polimer kendinden iletken özelliği sahip değildir fakat p-doping ile kısmi yükseltgenme, n-doping ile kısmi indirgenme sağlanır ve iletken hale gelir. Buna doplama denir iletken polimelein yapısını anlamak in önemlidir. Diğer önemli bir teori ise bant teorisidir. Elektron bantları arasındaki enerji farklılığı eğer yüksek ise bu banlar arasında elektron geçişi olmaz ve iletkenlik sağlanmaz. İletken polimerlerin sentezenmesi çeşitli kimyasal polimerizasyon yöntemleri ile sağlanır fakat çözünür iletken polimer sentezleme için subsütisyon ve kopolimerleşme çok önemlidir. Seryum amonyum nitrat ve tuzları iletken polimer sentezlemede çok önemli yükseltgen özellik gösteren bir kimyasaldır. Kokusuz sarıdan turuncu ya dönük renge sahiptir ve birçok organik çözücüde çok az çözünür. Oksidatif katılma fotooxidasyon nitrasyon ve graft polimerizasyon reaksiyonlarında çoklukla kullanılır. Kuvvetli bir yükseltgen olduğundan dolayı ceryum tuzları redox reaksiyonlarındada sıklıkla kullanılır. Bir redoks sisteminde başlama, yükseltgenme ve indirgenme aşamalarından oluşur. Bir redoks sisteminde Ce(IV) veya Mn(III) gibi bir yükseltgen ortamda buluna organik molekül ile reaksiyona girerek komplex oluşturur, dekompozisyona uğrayan komplex serbest radikal açığa çıkarır böylelikle polimerizasyon başlamış olur Blok kopolymer sentezi için tek yol redoks sistemi ile polimerizasyonu başlatmaktır. Düşük sıcaklık koşulunda sentez yapabilme imkanı

sunan redox sistemi yan reaksiyonlarıda elimine eder ve diğer metodlara üstünlük sağlar. Yan reaksiyonların azaltılması ile daha yüksek molekül ağırlıklı ürün elde edilmesi sağlanır. Seryum tuzlarının kullanıldığı redoks sistemlerinde bu fonksiyonel üstünlükler göze çarpar ve literaturde indirgen molekül olarak alkollerin ketonların ve asitlerin kullanıldığı görülmüştür

Redox polimerizasyon sisteminin seryum iyonu ile kullanılması özellikle iletken bir polimer olan poliprolün kimyasal olrak sentezlenebilmesine imkan sunar. Polipirol sahip olduğu kolay sentezlenebilme ve yüksek iletkenlik özelliklerinden dolayı en çok araştırılan iletken polimerdir. Polipirol sentetik olarak kolay sentezlenebilmesine rağmen çözücüler içinde çözünmeme ve kolay işlenememe özelliklerinden dolayı kullanım alanları azaltmaktadır. Polipirolün seryum amonyum tuzları ile sentezlenmesi çözünürlük özelliğini geliştirmektedir. İletken polimerler çeşitli yöntemlerle işlenebilir hale gelmiştir. Bu yöntemler solüsyon halinde hazırlamak, kimyasal olarak kompozit oluşturmak ve son olrak kopolmer ve graft kopolimer hazırlamak. Seryum amonyum tuzlarının redox reaksiyon sisteminde, sulu ortamda vinil polimerizasyonunu başlattığı daha önceki çalışmalarımızdan bilinmektedir. Sulu ortamda polimerizasyon (emülsiyon) reaksiyonunun teknik açıdan birçok avantajı bulunmaktadır. Sulu ortam reaksiyon sisteminde seryumla reaksiyona giren indirgen maddeler, glikoz, maltoz, karboksilli asit, hidroksi asit, aminoasit, amin tetra asetik asit, aminotri metilen fosfonik asit kullanılmıştır. Sulu ortam reaksiyonlarında deprotonasyona karşı gelişmiş stabilite sağladığı gibi daha gelişmiş termal stabilite ve termoaktif özellikler elde edilir. Ayrıca daha kompak ve düşük boyutlu polipirol eldesi sağlanır Elde edilen polipirolün çözünürlük özellikleinde gelişme olduğu raporlanmıştır.

Bu çalışmada pirol monomeri, seryum amonyum tuzu ve etoksi nonil fenol varlığında sulu ortamda redox polimerizasyonu ile polimerleştirilmesi sağlanacaktır. Etoksi nonil fenol yüzey aktif özellik gösteren organik bir bileşiktir. Ve alkil fenollerin bir üyesidir . Nonil fenol iki sekilde farklılaşır fenol grububunun substitue olması ile ve etoksi grubunun dallanmasıyla. Polipirol nonil fenol redox sistemi ile sentezlenmesi blok copolymer eldesi için çok uygun bir ortam sunmaktadır. Düşük sıcaklıklarda uygulanabilir redox sistemler yan reaksiyonların en aza indirilmesinde kolaylık sağlar. Reaksiyonun başlama aşamasında iki olasılık sözkonusudur ilk olarak Py radikal anyonu oluşur Ce(IV) nin ortamdaki radikali yükseltgemesi ile Py^+ katyonu

oluşur ve bu molekülün dimerize olması ile $2H^+$ açığa çıkar ve polimerizasyon reaksiyonu buradan devam eder. İkinici olasılık ise dimerize olacak Py radikalini proton kaybeder ve hem Ce(IV) / etilol redoks reaksiyonu hemde serbet radikal başlangıç aşamasında ortaya çıkmış olur. Bundan sonra gerçekleşen büyüme aşamasında zincir Py ve Ce(IV) tükenene kadar büyümeye devasm eder. Sonlanma aşamasında büyüyen polipirol zincirleri nonil fenol 30 etoksi radikali ile birleşebilir ve böylelikle PPy-b-ENP30 kopolimeri oluşmuş olur.

Monomer / oxidant (Pirol / Ce^{+4}) mol oranlarının, elde edilecek polimer verimi ve iletkenlik, çözünürlük gibi fiziksel özellikleri üzerindeki etkisi araştırılmıştır. Öncelikle ideal bir Ce^{+4} konsantrasyonu yapılan deneyler sonucunda bulunmuştur. Optimum iletkenlik ve verim gösteren bu konsantrasyon değeri sabit tutularak monomer pirolün konsantrasyon değeri değiştirilmiş ve oluşan kopolimerin iletkenlik değerine nasıl etki ettiği ölçülen iletkenlik değerleri ile saptanmıştır. Elde edilen polimerlerin spektroskopik olarak Fourier Transform Kızılötesi Spekrometresi ile molekülün yapsısında bulunan karakteristik polipirol nonil fenol etoksi ve Ce(IV) pikleri saptanmıştır ve literatür ile uyumludur. Ayrıca Taramalı Electron Mikroskopu ile karakterizasyonu yapılan numunelerde çok nonoboyutta partikül elde edildiği gözlenmiştir. Elde edilecek blok copolymerin çözünürlük iletkenlik gibi özelliklerinde gelişme sağlanması amaçlanmış ve yapılan deneyler sonucunda daha işlenebilir iletken polipirol kopolimeri eldesi sağlanmıştır. .Pirolün sulu ortamda, seryum ammonyum tuzunun nitrik asitli çözeltisi varlığında redox polimerizasyonu, oda sıcaklığında manyetik karıştırıcılı sistemde yapılmıştır Ayrıca sisteme aynı zamanda yüzey aktif madde özelliğine de sahip farklı etoksi grupları içeren nonil fenol eklenerek (nonil fenol 10 etoksi ve nonil fenol 30 etoksi) deneyler farklı mol oranlarında da yapılmış olup nonil fenolün sisteme olan etkisi incelenmiştir.. Hem seryum ammonyum tuzunun hemde etoksi nonil fenolün molar konsantrasyonundaki farklılığın polipirolün karakteristik özelliklerine yapacağı değişikliğin incelenmesi sağlanmıştır. Nonil fenolün Ce^{+4} ile oksidayon reaksiyonu vermesi ile pirol ve nonil fenol kimyasal olarak bağlanması sağlanmıştır polipirole kimyasal bağlı nonil fenol grubunun elde edilecek polimerin fiziksel özelliklerindeki etkisi incelenmiştir. ve iletkenlik değeri yaklaşık 10^{-3} olarak ölçülmüştür. Bu değer polipirolün iletkenlik değerinden küçük olmakla beraber daha işlenebilir bir yapı sunduğundan ileriki araştırmalara yol açmıştır.

1. INTRODUCTION

In recent years, intrinsic conducting polymers with conjugated double bonds have been attracted much attention as advanced materials. Among those conducting polymers, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis and higher conductivity than many other conducting polymers. PPy can often be used as biosensors , gas sensors , wires, microactuators, antielectrostatic coatings, solid electrolytic capacitor, electrochromic windows and displays, and packaging, polymeric batteries, electronic devices and functional membranes. PPy coatings have an excellent thermal stability and are good candidate for use in carbon composites [13]. Furthermore, the electrochemical process parameters affecting the properties of the PPy coatings are also investigated [14]. PPy can be easily prepared by either an oxidatively chemical or electrochemical polymerization of pyrrole.

However synthetically conductive PPy is insoluble and infusible which restricts its processing and applications in other fields. The problem has been extensively investigated and new application fields have also been explored in the past several years. For example, PPy-based polymers can be used to load and release drugs and biomolecules PPy-based polymer blends can protect the corrosion of metals. However, PPy is a hard, brittle, and nonprocessable solid that is insoluble in common solvents. The other method for improving the mechanical properties of PPy is the preparation of composites from a conducting polymer and an insulating polymer. This method improves the mechanical properties of PPy rather than the solubility properties. The oxidative polymerization of Py by ceric(IV) ammonium nitrate, in the presence of ketonic resins were studied and soluble PPy copolymers were produced. These soluble copolymers had conductivity values as high as 10^{-2} S/cm. Ce(IV) salt oxidized both Py and methylol groups of ketonic resins, and block copolymers were formed by the termination reaction of growing PPy radicals with the radicals produced in the ketonic resin by Ce(IV). [1,2] The polymerization of vinyl monomers with a redox initiator system of silicone tegomer and Ce(IV) salt resulted

in polymers with silicone tegomer chain ends. [3] Ce(IV) oxidized hydroxymethyl groups of silicone tegomers and yielded radicals that initiated the polymerization of vinyl monomers. [4] In this work, the oxidative polymerization of Py by ceric(IV) ammonium nitrate, in the presence of NPE was studied with the aim of producing copolymers with higher elasticity and higher solubility than PPy. The reaction mechanisim can be shown in Figure 1.1. The effect of the concentrations of Py, and Ce(IV) on the yield, conductivity, and physical properties of the product was investigated.

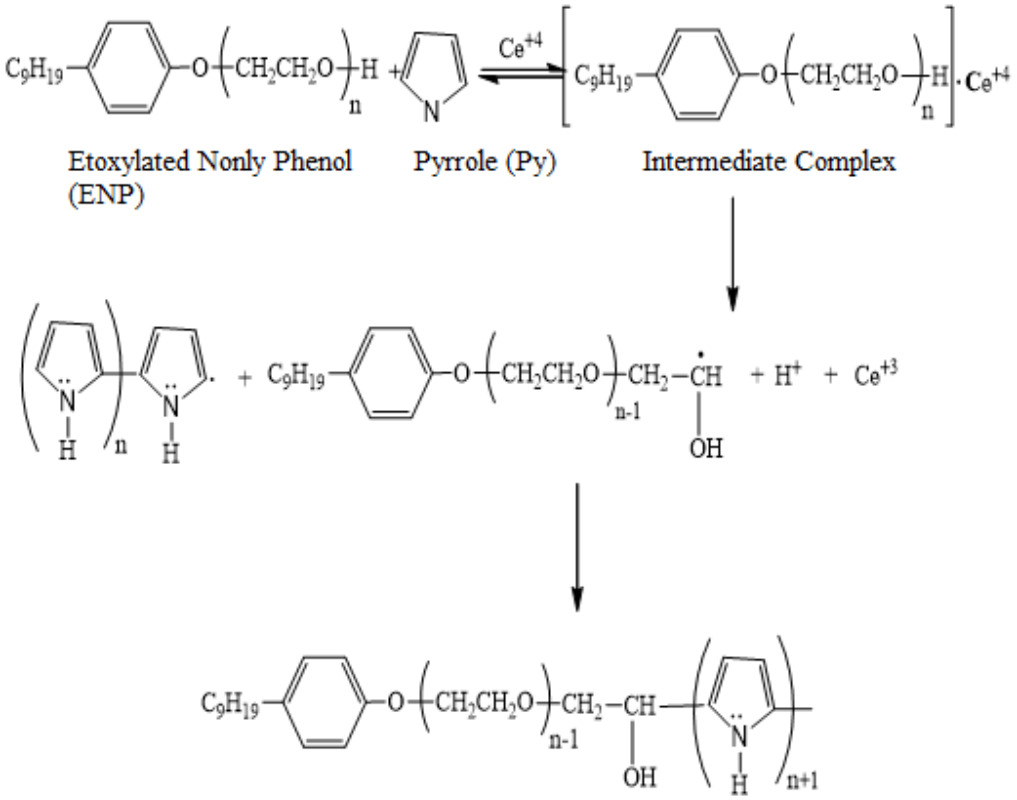


Figure 1.1: The formation of polypyrrole and ethoxylated nonylphenol copolymer.

2. THEORY

2.1 Conducting Polymer

Polymers have long been used as insulating materials. For example, metal cables are coated in plastic to insulate them. However, there are at least four major classes of semiconducting polymers that have been developed so far. They include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers.

The report of electrical conductivity in ionic polymers in 1975 [5] attracted considerable interest. Since then, various ionically conducting polymers or polymer electrolytes have been prepared for a wide range of applications ranging from rechargeable batteries to smart windows. Polymer electrolytes are also highly processable. The ionic conduction mechanism requires the dissociation of opposite ionic charges and the subsequent ion migration between coordination sites, which are generated by the slow motion of polymer chain segments. Consequently, polymer electrolytes normally show a low conductivity and high sensitivity to humidity. They often become electrically non-conducting upon drying.

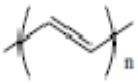
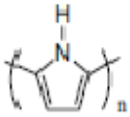
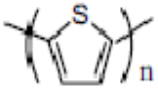
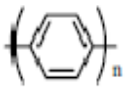
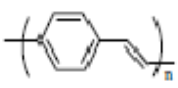
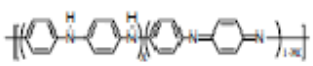
Along with all of the activities described above, various conjugated polymers have been synthesized during the past 25 years or so which show excellent electrical properties[6]. Owing to the delocalization of electrons in a continuously overlapped p-orbital along the polymer backbone, certain conjugated polymers also possess interesting optical and magnetic properties. These unusual optoelectronic properties allow conjugated polymers to be used for a large number of applications, including protecting metals from corrosion, sensing devices, artificial actuators, all-plastic transistors, non-linear optical devices and lightemitting displays.

Due to the backbone rigidity intrinsically associated with the delocalized conjugated structure, however, most unfunctionalized conjugated polymers are intractable like being insoluble, infusible and brittle. Some of them are even unstable in air.

2.1.2 Conjugated conducting polymers

Table 2.1 lists the repeat units and conductivities for some common conjugated polymers [7]. As can be seen in Table 2.1, the conjugated structure with alternating single and double bonds or conjugated segments coupled with atoms providing *p*-orbitals for a continuous orbital overlap seems to be necessary for polymers to become intrinsically conducting. This is because just as metals have high conductivity due to the free movement of electrons through their structure, in order for polymers to be electronically conductive they must possess not only charge carriers but also an orbital system that allows the charge carriers to move. The conjugated structure can meet the second requirement through a continuous overlapping of orbitals along the polymer backbone. Due to its simple conjugated molecular structure and fascinating electronic properties, polyacetylene has been widely studied as a prototype for other electronically conducting polymers [8].

Table 2.1 : Some conjugated conducting polymers.

Polymer (date conductivity discovered)	Structure	Conductivity (S/cm)
I. Polyacetylene and analogues		
Polyacetylene (1977)		$10^3 - 1.7\times10^5$
Polypyrrole (1979)		$10^2 - 7.5\times10^3$
Polythiophene (1981)		$10 - 10^3$
II. Polyphenylene and analogues		
Poly(paraphenylene) (1979)		$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		$3 - 5\times10^3$
Polyaniline (1980)		30 – 200

2.1.1.1 Doping

Since most organic polymers do not have intrinsic charge carriers, the required charge carriers may be provided by partial oxidation (*p*-doping) of the polymer chain with electron acceptors or by partial reduction (*n*-doping) with electron donors. Through such a doping process, charged defects as polaron, bipolaron and soliton are introduced, which could then be available as the charge carriers. In the case of I_2-doped *trans*-polyacetylene, it was estimated that nearly 85% of the positive charge is delocalized over 15 CH units to give a positive soliton. In fact, the insulator-to-metal transition in conjugated polymers is not so simple, and the way in which charges can be stabilized on the polymer chains and the nature of the charge transport process are still a matter of debate. Nevertheless, the simple band theory can provide some useful information about the dopinginduced changes in electronic structure.

According to band theory [9], the electrical properties of direct gap inorganic semiconductors are determined by their electronic structures, and the electrons move within discrete energy states called bands. By analogy, the bonding and antibonding p-orbitals of the *sp*2 hybridized electron materials generate energy bands, which are fully occupied and empty . The highest occupied band is called the valence band, and the lowest unoccupied band is the conduction band. The energy difference between them is called the band gap.

Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be electrically conducting, as neither empty nor full bands can carry electricity. Owing to the presence of partially filled energy bands, metals have high conductivities which can be shown in Figure 2.1. The energy bands of insulators and semiconductors, however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap. In contrast, conjugated polymers have narrower band gaps and doping can change their band structures by either taking electrons from the valence band *p*-doping or adding electrons to the conduction band *n*-doping. When an electron is added (removed) to the bottom of the conduction band(from top of the valence band) of a conjugated polymer.

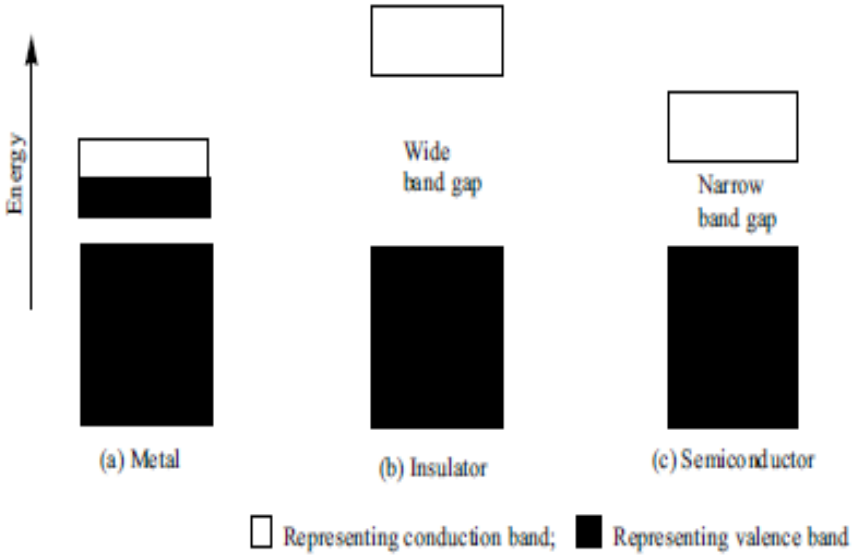


Figure 2.1: A schematic representation of energy gaps

The conduction (valence) band ends up being partially filled and a radical anion (cation), commonly termed as a polaron [10], is created .The formation of polarons causes the injection of states from the bottom of the conduction band and top of the valence band into the band gap. A polaron carries both spin (1/2) and charge. Addition of a second electron on a chain already having a negative (positive) polaron results in the formation of a bipolaron (spinless) through dimerization of two polarons, which can lower the total energy can be seen in Figure 2.2. In conjugated polymers with a degenerate ground state (i.e. two equivalent resonance forms), like trans-polyacetylene, the bipolarons can further lower their energy by dissociating into two spinless solitons at one-half of the gap energy. Solitons do not form in conjugated polymers with nondegenerate ground states, such as in polypyrrole, polythiophene and polyaniline [10] The population of polarons, bipolarons, and/or solitons increases with the doping level. At high doping levels, the localized polarons, bipolarons or solitons near to individual dopant ions could overlap, leading to new energy bands between and even overlapping the valence and conduction bands, through which electrons can flow. The bulk conductivity of conducting polymers should, in principle, consist of contributions from intra-chain, inter-chain and inter-domain electron transportations [11]. While the details for each of the transporting processes and their relative importance are still not fully understood, some of the factors that influence conductivity have been recognized.

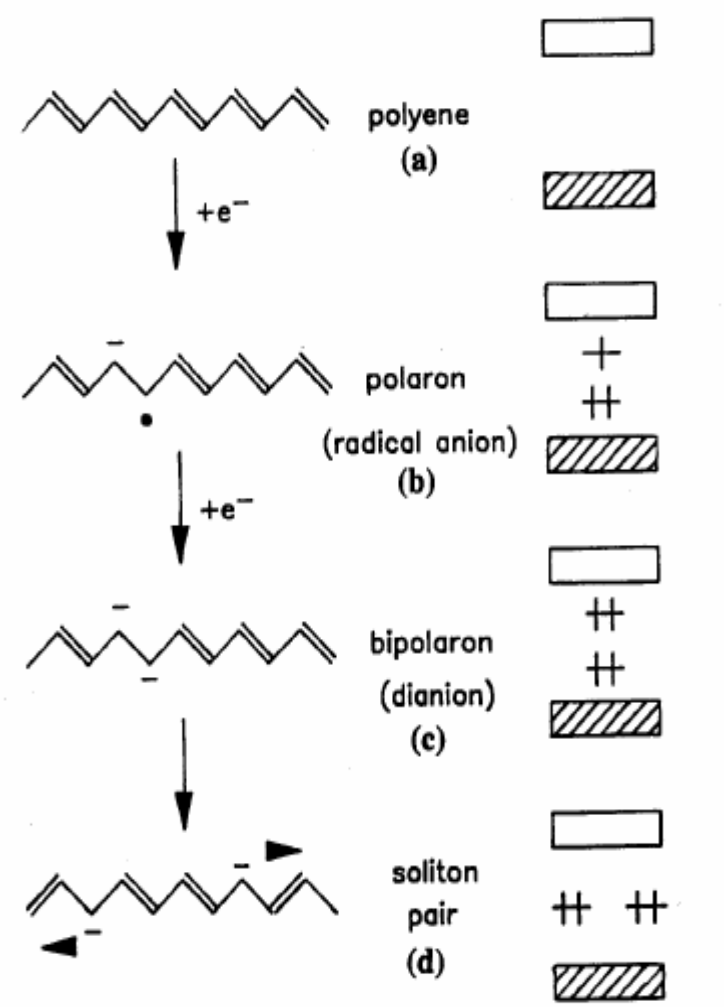


Figure 2.2: A schematic description of the formation of polaron, bipolaron, and soliton pair on a trans-polyacetylene chain by doping.

As can be seen from the foregoing discussion, the doping process is the most obvious factor which influences conductivity of conjugated polymers. Other factors include the orientation, crystallinity and purity of the conjugated polymers.

2.1.2 Sytnheses of conductive polymers

Although various catalyst systems can be used to initiate acetylene polymerization, the Ziegler-Natta catalyst remains the major one for chemical polymerization of acetylene [12] .

Particularly, the $Ti(OBu)_4/AlEt_3$ is a preferred catalyst system for producing linear polymers of high molecular weight, high crystallinity and high conductivity upon doping. In fact, before the early 1980s no conjugated conducting polymer had been shown to be soluble in any solvent without decomposition due to backbone rigidity associated with the delocalized conjugated structure.

Furthermore, most unfunctionalized conjugated polymers were found to be unstable in air [13] . Since then, a number of techniques have been developed to overcome these problems. Relatively stable conducting polymeric materials have been made, for example, by physically blending conjugated polymers with certain non-conjugated macromolecules [13] and chemically synthesizing conducting polymer colloids [14] or conjugated oligomers. On the other hand, many clever synthetic routes have now been devised for preparing processable conjugated polymers, as described below.

2.1.2.1 Syntheses of soluble conjugated polymers

By substitution

As is well known, both chemical and physical properties of a polymer material may change with substitution. Consequently, soluble forms of various conjugated polymers have been prepared by grafting suitable side groups and/or side chains along their conjugated backbones. Examples include polyacetylene, poly(phenylene vinylene) (PPV), polythiophene, polypyrrole and polyaniline grafted derivatives [15]. Soluble polypyrrole and polyaniline have also been synthesised by introducing alkyl side groups [16]. Grafting with hydrophilic side groups/chains (-SO_3H, -COOH, -OH, *etc*.) even allows the formation of watersoluble conducting polymers [17]. The high solubility of the substituted conjugated polymers is often gained at the expense of significantly reduced conductivity. For instance, the conductivities of substituted polyacetylenes, after doping, were shown to be lower than that of doped polyacetylene by several orders of magnitude [18] . Polyaniline coatings with a relatively high electrical conductivity, however, have been produced from soluble polyaniline emeraldine salt generated by the protonic doping of polyaniline emeraldine-base with organic sulfonic acids containing large organic groups [19,20].

By copolymerization

Copolymerization of conjugated polymers with various soluble segments provides an alternative way to circumvent the intractability of conjugated polymers. The combination of optoelectronic properties characteristic of conjugated structures and the solubility of the soluble polymeric segments into a single copolymer chain should, in principle, lead to a material with properties characteristic of both the constituent components.

2.2 Ceric Ammonium Nitrate (CAN)

Most reagents play a single role in chemical reactions of various types. Ceric ammonium nitrate is an orange solid and commercially available. It has been widely used in industry and academia during the past six decades. In this review, the role, efficiency, and advantages of ceric ammonium nitrate are discussed for its use with versatile roles in different chemical transformations. These reactions include carbon–carbon bond formation, oxidative carbon– carbon bond cleavage, nitration, and removal of protecting groups. The information will be of value to chemical synthesis of new compounds and materials.

In 1936, Smith [21] invented a new chemical agent ceric ammonium nitrate (CAN), which is also named ammonium cerium(IV) nitrate, ammonium hexanitratocerate(IV), or ammonium nitratocerate(IV). It is prepared from fresh ceric hydrate or oxide in an excess amount of nitric acid and then with a quantitative amount of ammonium salt. Crystallized CAN in orange colour can be obtained by evaporation of the solvent at low temperatures. X-Ray crystallography of CAN shows that cerium(IV) locates at the center of the anion complexed by six bidentate nitrate groups [22]. Thus the formula can be written as $(NH_4)_2[Ce(NO_3)_6]$. Being anon-hygroscopic solid, this reagent is readily available in pure form and can be handled easily. The solubility of CAN in water is 1.41 g/ml at 25°C and 2.27 g/ml at 80°C [23]. It is to a smaller extent in polar organic solvents, such as acetic acid. In redox reactions, CAN functions as an oxidant. Its consumption can be judged by colour change from orange to pale yellow or colourless if the substrate and the product are not strongly coloured. Because of its extremely limited solubility in common organic solvents, reactions involving CAN are often carried out in mixed water–organic solvents, such as aqueous acetonitrile. The toxicity of CAN has not been elucidated. In industry, solution of CAN in dilute perchloric acid is used as etchants for preparation of printed circuits, metal samples, and for surface cleaning prior to fabrication by soldering. This blend is particularly useful in the etching of alloys, monel, nichrome, and stainless steel. In academia, CAN is explored extensively in organic reactions. Representative examples include oxidation oxidative addition, photooxidation, nitration, deprotection, graft polymerization. Intermediates formed in these reactions may undergo oxidative fragmentation, rearrangement, or cleavages of C–H and C–C bonds. In the Third World, many

research groups successfully developed useful transformations by application of this reagent. For example, Chavan and Subbarao [69] developed a CAN-mediated azidoalkoxylation of enol ethers and olefins shown in Figure 2.3. Polanc [70] established a selective conversion of hydrazides to esters by using CAN in the presence of alcohol shown in Figure 2.4. Markó [50] applied CAN as a catalyst in the deprotection of acetals to give the parent ketones shown in Figure 2.5. Arslan and Hazer [60] reported a polymerization of methyl methacrylate initiated by CAN in combination with polytetrahydrofuran diol which can be shown in Figure 2.6.

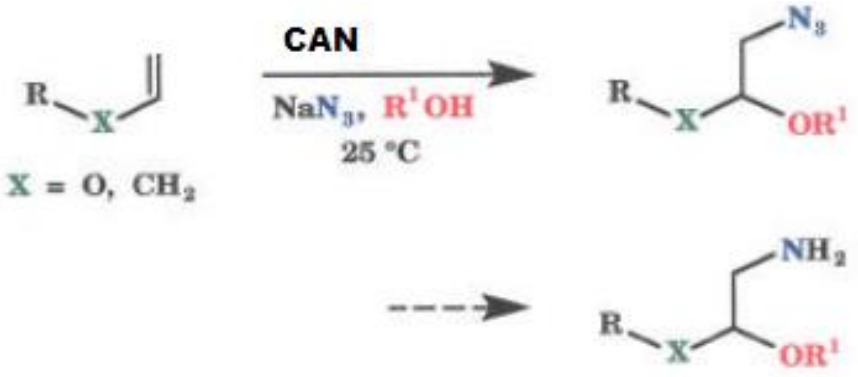


Figure 2.3 : CAN-mediated azidoalkoxylation of enol ethers and olefins.

Figure 2.4 : Selective conversion of hydrazides to esters.

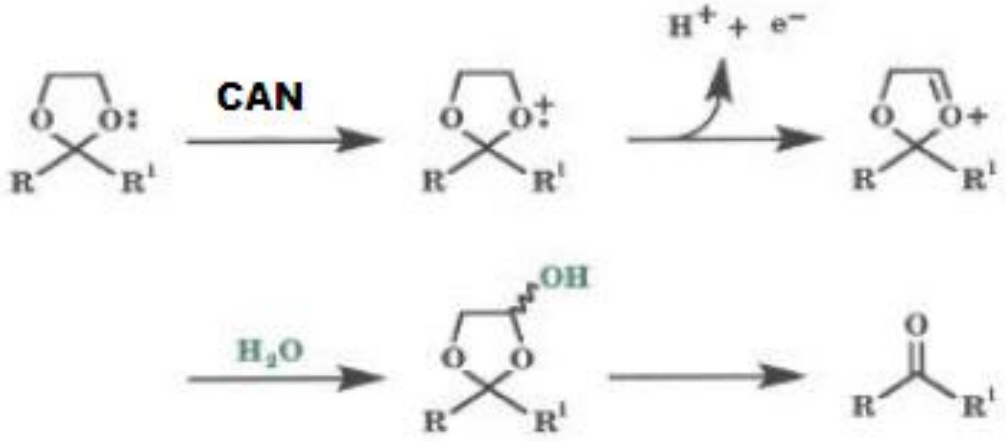


Figure 2.5 : CAN as a catalyst in the deprotection of acetals.

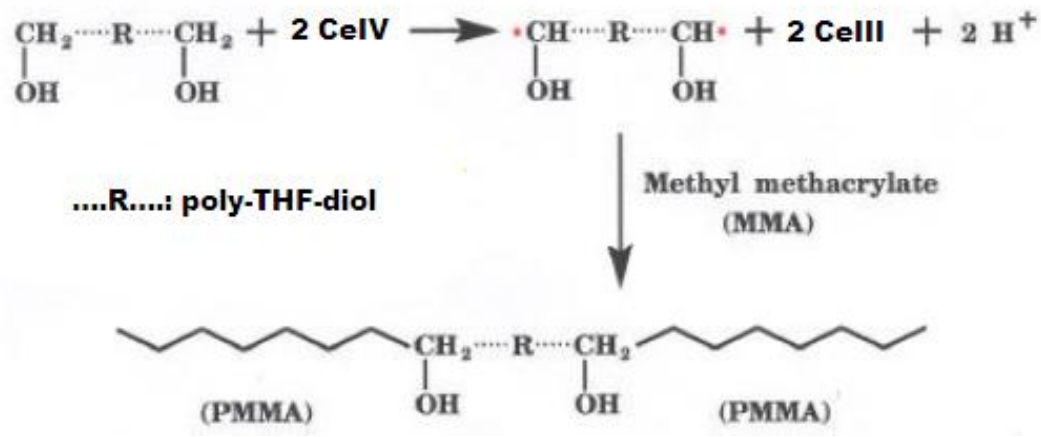


Figure 2.6 : Methyl methacrylate initiated by CAN.

2.3 Redox Systems

Polymerizations initiated by a reaction between an oxidizing and a reducing agent are called redox polymerizations. The essence of redox initiation is a reduction-oxidation process. In this process an oxidant such as Ce(IV) or Mn(III) forms initially a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization. Commonly used oxidants include peroxides, persulphates, peroxydiphosphate, and the salts of transition metals. These oxidants form effective redox systems with various reducing agents like alcohols, aldehydes, amines, thiols for the aqueous polymerization of vinyl monomers. The essential features of components constituting a redox pair for aqueous polymerization are their solubility in water and fairly fast and steady liberation of active radicals [28] Apart from the fact that low temperatures can be employed with redox systems, the reaction rate is easy to control by varying the concentration of metal ion or peroxide [29]. There are many reports in the literature on the block copolymer synthesis. Initiation by a redox process is only a method to obtain these types of polymers [30-33]. However, initiation by a polymer having functional end groups attached to the chains, resulting from redox polymerization has not been investigated widely in the literature [34,35].

The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions are minimized [36]. This method has found wide applications in initiating various polymerization reactions [37,38] and with industrial

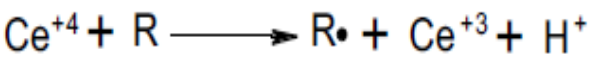
importance, e.g. low-temperature emulsion polymerizations [39,40].

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation states in an aqueous medium can provide valuable information regarding the mechanistic details of the elementary steps [41]. Besides the very short induction period (almost negligible), a lower energy of activation (40-80 kJ/mol) allows the redox polymerization to be carried out under milder conditions than thermal polymerization. This lowers the possibility of side chain reactions giving high molecular weight polymers with a high yield [40]. There are still some problems with this redox system, namely a poor solubility of such inorganic salts in a medium (acrylic resin), the formation of slightly colored products and an expected short pot-life due to the fact that polymerization may occur already at ambient temperature [42]. Various redox systems, such as ceric, manganese, cupper, iron, vanadium ion, and hydrogen peroxide, have been used as catalysts for synthesis block copolymers via redox polymerization. Ceric-based catalysts seem to be the most versatile. The redox systems including various catalysts have also been investigated.

2.4 Ceric Ion Redox Polymerization Systems

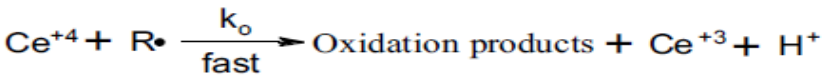
Ceric ions in acidic media are well-known oxidizing agents for various organic substrates [43]. Also, these ions, either by themselves or in combination with reducing agents function as initiators for vinyl polymerization. A first attempt to initiate polymerization [44-51] by Ce(IV) in organic solvents was performed in 1979 by Singh et al. [52] who observed that the solvent toluene inhibits the redox initiating process for the polymerization of acrylonitrile. The suitable reducing agents reported in the literature are alcohols [53], polyoils [54], ketones [55], acids [56], amines [59], thiols [57], and thiourea [58]. Based on the experimental results, the following kinetic reaction schema are proposed by Nagarajan et al. [60] for vinyl radical polymerization.

I. **(a)** Reaction of ceric ion with reducing agent:

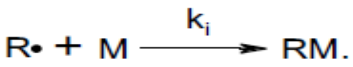


Where, R is reducing agent and R. is the organic free radical formed from the reducing agent.

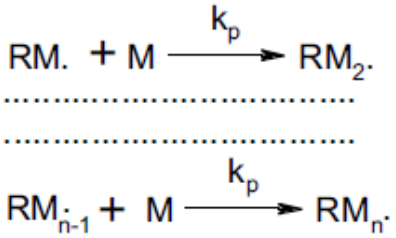
(b) Reaction of the radical with Ce^{+4} to give the oxidation products:



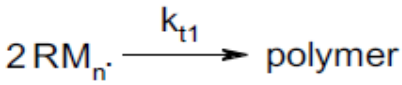
II. Initiation of polymerization by reaction of the free radical with monomer:



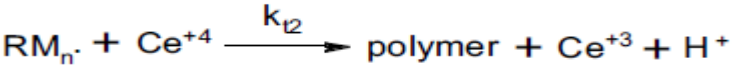
III. Propagation:



IV. **(a)** Mutual termination:



(b) Linear termination by Ce^{+4} :



2.5 Synthesis of Polypyrrole

Polypyrrole (PPy) can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer can be shown in Figure 2.7. The polymer has resonance structures that resemble the aromatic or quinoid forms. In this neutral state the polymer is not conducting and only becomes conducting when it is oxidized. The charge associated with the oxidized state is typically delocalised over several pyrrole units and can form a radical cation (polaron) or a dication (bipolaron). The charge

associated with the oxidized state is typically delocalised over several pyrrole units and can form a radical cation (polaron) or a dication (bipolaron).

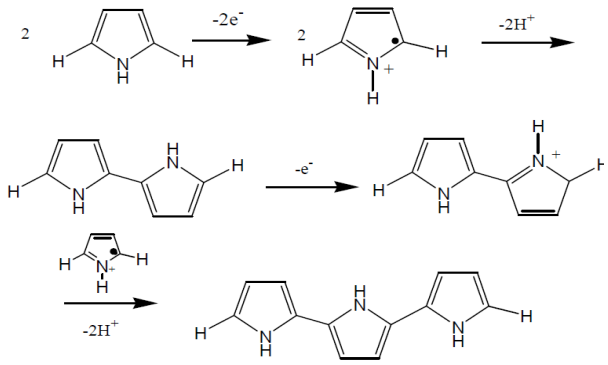


Figure 2.7 : Oxidative polymerization of pyrrole to polypyrrole proceeds via a one electron oxidation of pyrrole to a radical cation, which subsequently couples with another radical cation to form the 2,2'-bipyrrole. This process is then repeated to form longer chains.

The final form of polypyrrole is that of a long conjugated backbone as seen in Figure 2.8. The charge associated with the oxidized state is typically delocalised over several pyrrole units and can form a radical cation (polaron) or a dication (bipolaron). The physical form of polypyrrole is usually an intractable powder resulting from chemical polymerization and an insoluble film resulting from electropolymerization.

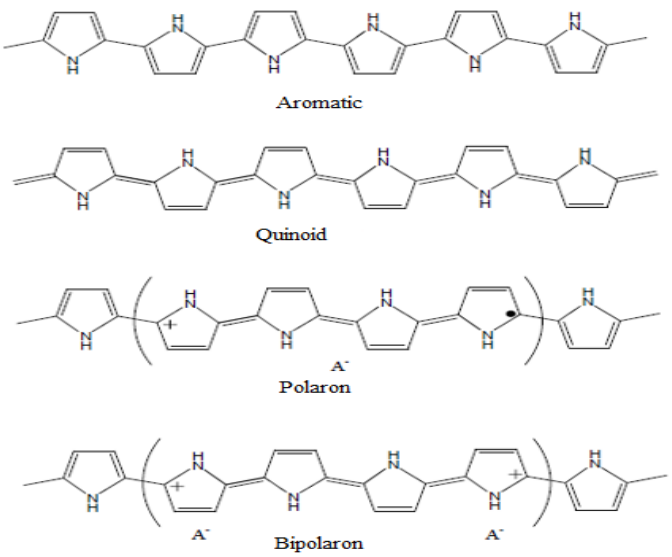


Figure 2.8 : Chemical structures of polypyrrole In neutral aromatic and quinoid forms and in oxidized polaron and bipolaron forms.

2.5.1 Chemical polymerization of pyrrole

Chemical synthesis of polypyrrole proceeds via the oxidation of pyrrole with an oxidant such as ferric chloride. The mechanism is similar to that for electropolymerisation of pyrrole and conductivities are comparable. The resulting polymer in its oxidized form is conducting with charge compensation afforded by $FeCl_4^-$. The conductivity of polypyrroles formed from different ferric salts (effect of dopant ion) has been related to the Fe^{2+} /Fe^{3+} redox potential with strong acid anions providing the most oxidizing ferric species. Weaker acid anions typically coordinate Fe^{3+} ions more strongly, reducing its oxidizing potential.[61] An investigation into the ferric ion equilibria in aqueous solutions showed that above a concentration of 0.5 M $HClO_4$ there was no change in the amount of available $Fe(H_2O)_6^{3+}$[62].

The solvent the reaction occurs in also changes the redox potential. For example the Fe^{2+} /Fe^{3+} redox potential is lower in water than acetonitrile. If the redox potential is too high, an irreversible dissolution of polypyrrole can occur, as for ferric perchlorate in acetonitrile.[63] Methanol has been found to produce the best conducting polymer based on conductivity and morphology.[64,65] The conductivity was related to the redox potential of the Fe^{2+} /Fe^{3+} system and could be varied by adding $FeCl_2$. The optimum redox potential in methanol was +0.5 V vs SCE. The solvent also has an influence on the dopant ion that remains in the PPy film. In ether using $FeCl_3$ as oxidant leaves $FeCl_4^-$ as the dopant ion, while in methanol, the dopant is mainly Cl- with some $FeCl_4^-$.[61] Water was found to be trapped in the PPy with formation of pyrrolidinone rings at chain terminations similar to electrochemically produced films.[61] Other counter ions to the ferric ion will also be incorporated into the PPy film[61] as will ions present in solution. Dopants whose bonds are labile such as Cl-O, B-F, P-F, should be avoided for sake of polymer stability.[66] Polymerisation of pyrrole in the presence of surfactants such as dodecylbenzyl sulphonic acid or a salt like sodium dodecyl sulphate, leads to an increase in mass yield due to incorporation of the salt/surfactant into the polymer.[67] Cationic surfactants were found to inhibit the polymerization of pyrrole. Polymerisation of pyrrole in the presence of polystyrene sulphonate (PSS) produced particles (non-colloidal) with the size being inversely proportional to the concentration of ferric chloride oxidant.[68] The size effect is due to the affinity of pyrrole and the ferric ion to PSS. The acid concentration affects the polymerisation process. The conductivity of polypyrrole

increases as the synthesis temperature is reduced. This is thought to be due to a reduction in the number of side reactions. Polypyrrole's conductivity as a function of temperature is studied as well as reflectivity, and classified into metallic, critical and insulating regions.[69] The density of polypyrrole has been determined to be 1.48 g cm-3 and 1.44 +/- 0.05 g cm-3.[68,70] Polypyrrole derivatives have been prepared and their properties studied. By blocking the 3,4- positions on the pyrrole ring, unwanted side reactions at these sites are eliminated. This has been noted to yield higher conductivity in the case of poly 3,4- dimethoxypyrrole.[71,72] Various alkylenedoxypyrroles have been synthesised and studied including a series of soluble species.[71,73,74] N-substituted pyrroles tend to induce twisting relative to adjacent pyrrole rings, thus limiting the conjugation length and conductivity. Solid state NMR has been used to elucidate some of the conducting mechanisms and structures.[75] Bipolarons appear to be the charge carriers and conductivity is linked to the loss or decomposition of the dopant ions. Elevated temperatures in air reduce the quinoid content and oxidise the 3,4-positions. Dodecyl sulphate is less stable than p-toluene sulphonate at elevated temperatures. Under argon the dodecyl sulphate doped film become brittle indicating cross linking at elevated temperatures.[75] The polymer produced by electrochemical or chemical synthesis is generally an intractable solid or powder. The next section presents some of the strategies that have been investigated for the purpose of producing useable material.

2.5.2 Electropolmerization of pyrrole

Electrochemical oxidation of pyrrole forms a film of conducting polymer at the electrode surface. Initiation: Formation of monomer radical cation by electrochemical oxidation, +0.8V vs SCE. Propagation. Combination of two radical cation monomers (or oligomers) followed by loss of two hydrogen ions. The linkage formed is at the 2 position of the pyrrole ring, forming 2,2'-bipyrrole. 2,5-disubstituted pyrroles do not polymerize and 2-monosubstituted pyrroles only form dimmers. Propagation: continues by re-oxidation of the bipyrrole and further combination of radicals. Termination: Occurs when no further monomer is present for oxidative polymerization or side reactions terminate the PPy chain.

An example of a termination reaction is the reaction with water to form the amide group. The success of electropolymerisation of pyrrole is due to the stability of the

radical through charge delocalization, and the ease of electro-oxidation. The loss of the hydrogen ions makes the dimer (oligomer) formation irreversible so proton acceptors, such as water, pyridine and bases, enhance electropolymerisation. Good solvents for electropolymerisation[61] include water, acetonitrile, butanone, propylene carbonate, (DMF) and ethanol though the presence of a bit of water (1 v/v%) enhances the polymer formation. Water can also result in chain termination. Potentiostatic, potential cycling, and galvanostatic methods can be used to electropolymerise pyrrole. Potentiostatic methods (constant potential) and cycling the potential yield the most consistent films of about the same quality. Galvanostatic deposition (constant current), does not produce as good a quality film as the other methods, but is useful for controlling film thickness. Electrochemical oxidation of a 5-member pyrrole oligomer[76] shows two reversible one-electron oxidation processes at Eo = -0.28 and -0.08 V vs Ag/Ag+. These correspond to the formation of the radical cation and dication, respectively, which are stable and do not polymerize. Another oxidation peak at Ep=0.75 V marks the start of polymerization. Extrapolation of the Eo value to infinite chain length for the first one electron oxidation gives a value of –0.59 V, compared to the measured value of –0.57 V for polypyrrole from the pentamer.[76] AFM studies of polypyrrole production indicate that time and substrate influence the final film morphology. Supporting electrolyte was found to affect deposition kinetics. Cyclic voltametry and NIR-Vis spectroscopy have also been used to show the affect of pH and counter ion. Neutral polypyrrole is noted to be very unstable in water or air. In basic solutions the polymer was doped with hydroxide ions and other anions in acidic solutions.

2.5.3 Recent studies of polypyrrole synthesis

The most important Polypyrrole Synthesis is Paal-Knorr Pyrrole Synthesis which is shown in Figure 2.9.

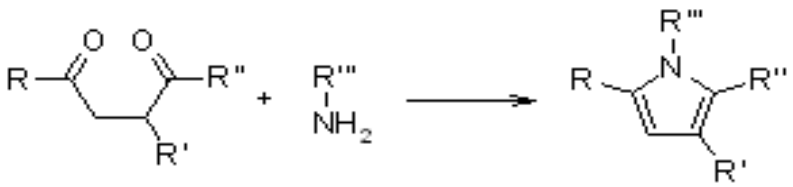


Figure 2.9 : Paal-Knorr pyrrole synthesis.

The use 10 mol % of $Cu(OTf)_2$ enables the coupling of α-diazoketones with β-enaminoketones and esters to yield 2,4,5-trisubstituted pyrrole derivatives. A wide range of 2,3-disubstituted indole derivatives were also prepared from α-diazoketones and 2-aminoaryl or alkyl ketones. The reaction mechanisim is shown in Figure 10. [77]

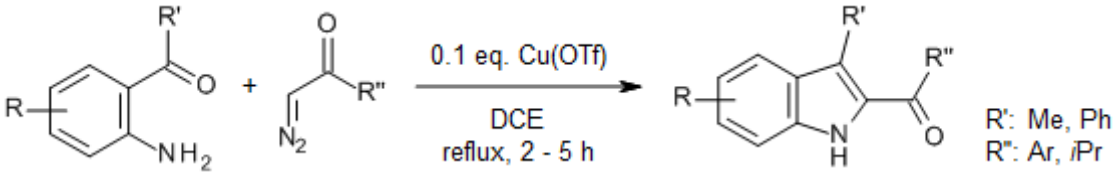


Figure 2.10 : The reaction mechanisim of 2,3-disubstituted indole.

A method for the preparation of *N*-acylpyrroles involves condensation of carboxylic acids with 2,4,4-trimethoxybutan-1-amine, followed by acid-mediated cyclization to form the pyrrole ring can be seen in Figure 2.11. The preparative procedure is highly tolerant of various functional groups. [78]

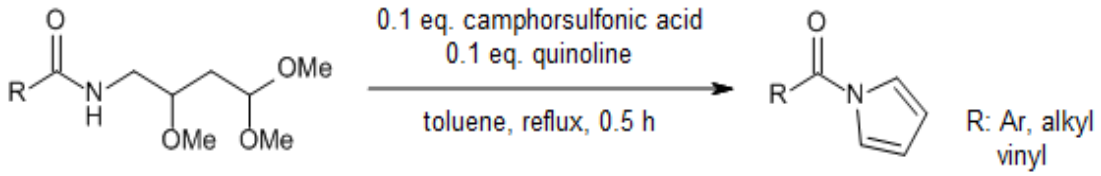


Figure 2.11 : The reaction mechanisim of condensation of carboxylic acids with 2,4,4-trimethoxybutan-1-amine.

Copper or nickel catalyzed highly selective denitrogenative annulations of vinyl azides with aryl acetaldehydes afford 2,4- and 3,4-diaryl substituted pyrroles depending on the selection of the transition metal catalyst. Compared with the reported acidic or basic conditions for polysubstituted pyrrole synthesis, the reaction conditions are mild, neutral, and very simple without any additives.

2.5.4 Properties of pyrrole

2.5.4.1 Acidic properties

Due to participation of N lone pair in aromaticity), pyrrole has exceptionally strong acidic properties. It can react with strong bases or Grignard reagent or potassium

metal in inert solvents, and with sodium amide in liquid ammonia, to give salt-like compounds which can be used to alkylate or acylate the nitrogen atom as shown in Figure 2.12.

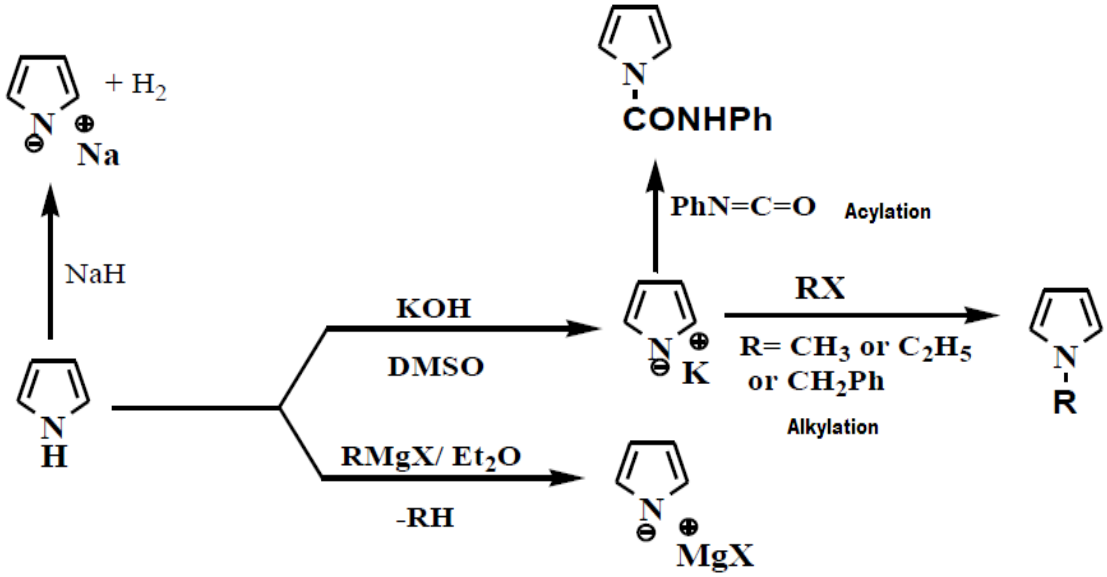


Figure 2.12 : Grignard reagent or potassium metal in inert solvents, and with sodium amide in liquid ammonia, to give salt-like compounds which can be used to alkylate or acylate the nitrogen atom.

Pyrrole is sensitive to strong acids. This is due to protonation occurs at one of C-3 and the resulting protonated molecule will add to another unprotonated pyrrole molecule this continues to give pyrrole trimer. This reaction is considered as electrophilic addition to pyrrole.

2.5.4.2 Reactions of pyrrole

Substitution at nitrogen,

1. Metallation of Pyrrole
2. Formation of N-substituted pyrrole

N-substituted products are normally isolated only from reaction of pyrrole anions with electrophiles display in Figure 2.13.

2.5.4.3 Electrophilic substitution in pyrrole

As expected for aromatic compound, pyrrole can react by electrophilic substitution. In comparison to benzene pyrrole is more reactive thus the substitution is easier and milder reagents can be used.

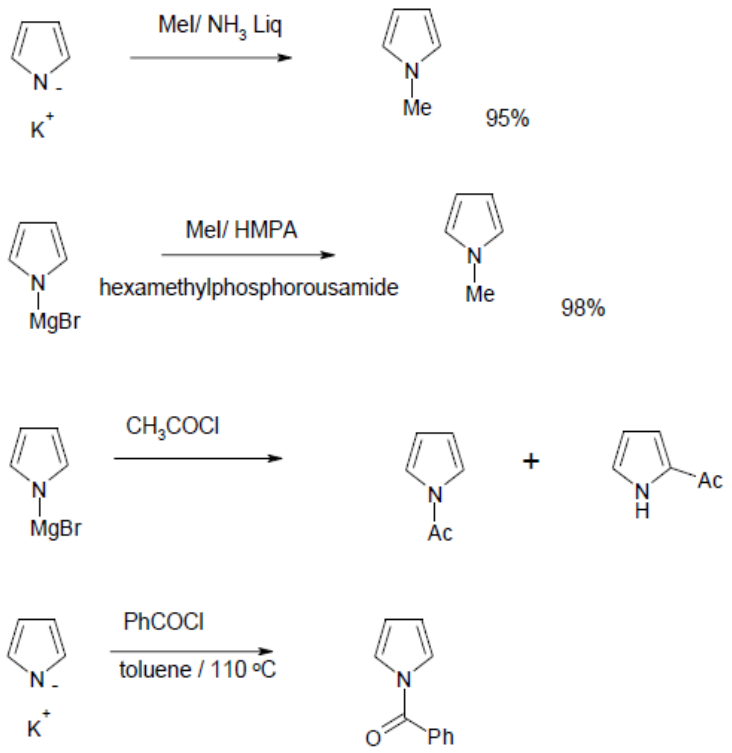


Figure 2.13 : The reactions of pyrrole anions with electrophiles.

The increased reactivity is a result of resonance which pushes the electrons from the N-atom into the ring making the c-atoms of pyrrole ring more electron rich than in case of benzene. In fact pyrrole resembles most reactive benzene derivatives (phenols and amines). These substitutions take place by an initial electrophile addition, followed by a proton loss from the "onium" intermediate to regenerate the aromatic ring.

Consequently, there are some modifications in usual electrophilic reagents, for instance, sulphonating and nitrating reagents have been modified to avoid the use of strong acids (induce polymerization). Also reaction with halogens requires no Lewis acid.

2.5.4.4 Orientation of electrophilic substitution in pyrrole

Electrophilic Substitution Reactions of Pyrrole Electrophilic substitution normally occurs at a carbon atoms instead of at the nitrogen. Also it occurs preferentially at C-2 (the position next to the heteroatom) rather than at C-3 (if position 2- is occupied it occurs at position 3).This is due to attack at C-2 gives more stable intermediate (it is stabilized by three resonance structure) than the intermediate resulted from C-3 attack (it is stabilized by two resonance structure) seen in Figure 2.14.

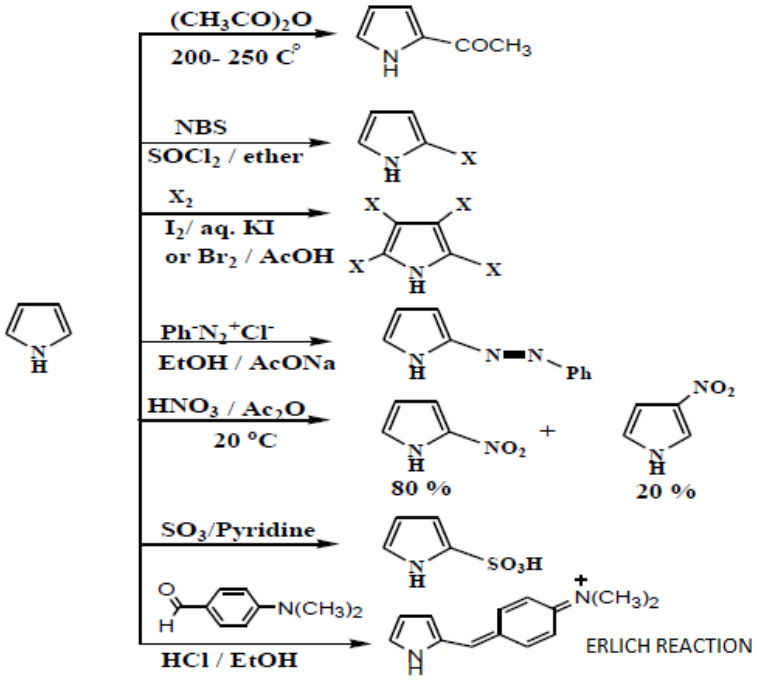


Figure 2.14 : Electrophilic Substitution Reactions of Pyrrole.

2.6 Processability of Polypyrrole

Researchers have been looking at a number of methods for making conducting polymers practical[79]. The trade off is often lower conductivities, though sometimes there is the serendipitous gain of stability. Some of these methods include direct polymerisation onto polymers sheets, glass, polymer and inorganic particles, clays,zeolites, porous membranes, fibres and textiles and soluble matrices. The methods used to coat these materials are reviewed below to highlight potential avenues for the development of radar absorbing materials

2.6.1 Solutions

The solubility of polypyrrole is limited due to its rigid structure and cross-linking.Attempts at increasing the solubility have been made by derivatizing the pyrrole ring at the 3- and 4- positions with alkyl groups, or substituents on the pyrrole's nitrogen. Another techniques that has been proven successful for some conducting polymers is to use long chain surfactant dopants like sodium dodecyl benzene sulfonate, di(2-ethylhexyl) sulfosuccinate sodium salt, or polystyrene sulfonate.[68] These polymers are then soluble in m-cresol, NMP, DMSO, DMF and THF.

2.6.2 Composites-chemical preparation

Since polypyrrole is generally intractable, attempts have been made to polymerize pyrrole onto or into the material where it is desired. In one strategy, the oxidant is mixed with the substrate and then exposed to pyrrole. For instance, ferric chloride has been mixed with polyvinyl alcohol, polyvinyl acetate, polyethylene oxide, poly(styrene-butyl acrylate-hydroxethyl acrylate), poly(methyl acrylate-co-acrylic acid), or rubber and exposed to pyrrole vapours. The variation of this method is to soak the substrate with the pyrrole monomer and then immerse it in an oxidant solution. Polypyrrole can be deposited directly onto a substrate surface, by placing the object in a solution containing pyrrole and oxidant. This coating strategy has been applied to fabrics and is discussed in greater detail below. Surfaces have been derivatised with dopant groups to facilitate polypyrrole-substrate adhesion and deposition. Low density polyethylene has been sulphonated and used as a template for the polymerisation of pyrrole yielding PPy layers up to 80 nm thick and conductivity up to 150 S/cm. A similar system was investigated using a sulphonic acid derivative of polystyrene grafted polyethylene, and compression molded sulphonated polystyrene objects. Other researchers have attempted to improvedeposition and adhesion of the polypyrrole by graft polymerisation of other polymersto the polyethylene. Polypyrrole has been deposited onto acrylic, polystyrene,polyimide and polyurethane foam. Composites have been made by dispersing polypyrrole powder in melted LDPE, HDPE and PS,or by dispersing polypyrrole powder or flakes in silicone rubber or vinyl ester and curing the material. Colloidal PPy has been made by stabilisation with methylcellulose. The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. PPy is attractive as an electrically conducting polymer because of its relative ease of synthesis. In order to exploit this material in some potential commercial applications, it will be necessary to synthesize it at low cost. The electrical conductivities of various composites produced under different reaction conditions were measured on pressed pellets of the composite powders. Polypyrrole and its composites were prepared chemically using FeCl3 as an oxidant in aqueous and non-aqueous media. The effect of various solutions such as water, ethylacetate, acetonitrile,methylacetate, methanol, ethylmethylketone and surface active agents, poly (ethylene glycol) and poly(vinyl acetate) on the properties of product were

studied. The results show that conductivities of the pressed pellets were in the range of ($2.2x10^{-3}$ - $4.4x10^{-1}$ S cm^{-1}) without additive, ($2.1x10^{-4}$ -$17.8x10^{-2}$ S cm^{-1}) with PEG and ($1.7x10^{-4}$-$8.2x10^{-2}$ S cm^{-1}) with PVAc respectively. The electrical conductivity is dependent on type of solutions and additives. PEG and PVAc are stabilizing agents and could affect the size, morphology and the homogeneity of particles because the surfactants are adsorbed physically to the polymer by the growing polymer. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters. The use of specific solvents during the processing plays an important role in the conductive properties of prepared films[80].

2.6.3 Copolymers and graft copolymers

Processable or soluble polypyrrole has been formed by graft copolymerisation of pyrrole. This has been accomplished by coupling pyrrole to a reactive monomer, polymerizing the monomer and then polymerizing the pyrrole as was done for methylmethacrylate, or derivitization of a preformed polymer with pyrrole and then polymerizing the pyrrole as has been done for polystyrene-co-poly (chlorostyrene). These materials were initially soluble with a tendency to become insoluble at high pyrrole content.

Direct copolymerization of pyrrole with other monomers has produced soluble conducting product. Examples include the polymerisation of pyrrole with various aniline derivatives, and methyl ethyl ketone formaldehyde resin [1].The conductivity and solubility depends on the feed ratio of pyrrole.

Random copolymers have been synthesized in high yields by chemical oxidative polymerization of aniline-pyrrole comonomers using H_2O_2 in the presence of Fe catalyst can be seen in Figure 2.15, Figure 2.16.[81].

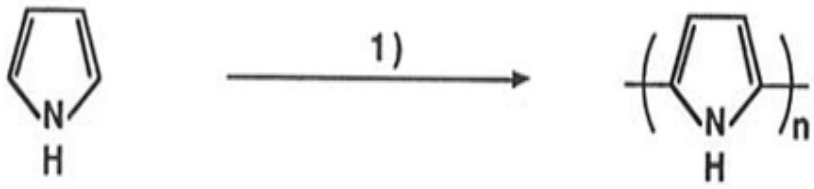


Figure 2.15 : Polymerization of pyrrole. H_2O_2 and Fe^{2+}, at 30 C in an aqueous H_2SO_4 solution.

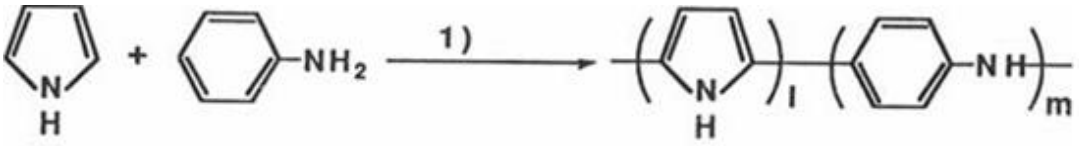


Figure 2.16 : Copolymerization of pyrrole and aniline. H_2O_2 and Fe^{2}+, at 30 C in an aqueous H_2SO_4 solution.

2.7 Ceric Ion and Pyrrole

As Ce (IV) is capable of vinly polymerization effectively .The polymerization of pyrrole become attractive by the use of strong oxidant such as Ce (IV) ions, means cerium ammonium nitrate (CAN) and Ceric (IV) sulphate. The reaction mechanisim can be seen in Figure 2.17. Increas in CAN/pyrrole concentration cause a linear increas in yield. [82]

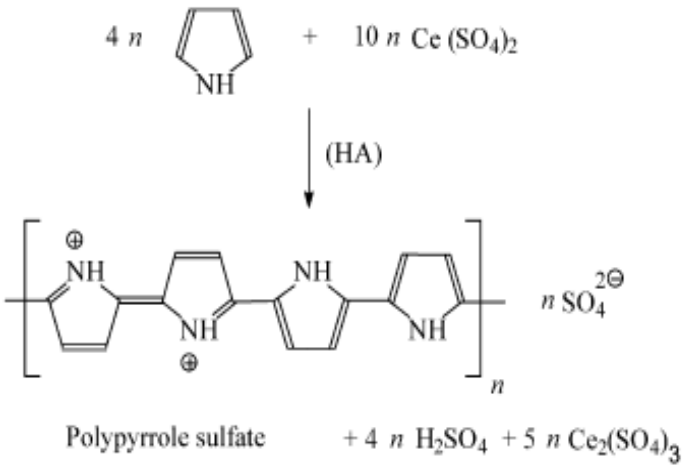


Figure 2.17 : The oxidation of pyrrole with cerium(IV) sulfate yields the corresponding polymers. HA is an arbitrary acid.

2.7.1 Pyrrole copolymer with ceric ion

Functional groups on the carbon or nitrogen atoms of the pyrrole ring were previously produced and polymerized to give derivatives of polypyrrole (PPy), and thus significant progress toward processibility and solubility of PPy derivatives has been made [83]. For example, 3-butyl sodium sulfonate pyrrole polymers and poly(3-alkylpyrrole) are soluble in some common organic solvents.[84,85] Because of the presence of 3,4- alkyl substiuents, the crosslinking is hindered, and the processibility of poly(3,4-dimethylpyrrole) is greater than that of PPy [86].

The copolymerization of pyrrole with other monomers or oligomers also produces copolymers with various properties. [86] For example, pyrrole/1-methylpyrrole copolymers have higher air and thermal stability than that of PPy. [87] Soluble and conductive polypyrrole copolymers have recently been produced with chemical oxidative polymerization with $(NH_4)_2Ce(NO_3)_6$ by using methyl ethyl ketone–formaldehyde resin [1] and silicon tegomers.[2] Their conductivities vary from 10^{-6} to 6 S/cm, depending on the polymerization parameters such as the mole ratio of resin/pyrrole, the addition order of components, the concentration of Ce(IV), and the structure of the resin. This article reports on the synthesis and polymerization of 1-hydroxyalkylpyrroles and their tosylated and octanoate ester derivatives, to produce conductive polymers. The effect of the substituted groups and the polymerization conditions on the conductivity and solubility of PPy copolymers were examined.

1-Hydroxyalkylpyrroles and their derivatives were chemically polymerized and copolymerized with pyrrole using $(NH_4)_2Ce(NO_3)_6$ and the physical properties, such as solubility and conductivity of the copolymers, could be changed by the type.

PPy was produced by the polymerization of pyrrole Py with Ce^{4+} salts [82]. The redox reaction between Py and Ce^{4+} produces pyrrole radical cation (Py+) which may dimerize with the expulsion of $2H^+$. The polymerization continues as long as Ce^{4+} and Py are available in the system[88].

Ketonic resin [1] and α,ω-dihydroxy polydimethylsiloxane (DH˙PDMS) [3] were included into the system of polymerization of Py with Ce^4+ salt in order to produce soluble and conductive copolymers of PPy can be seen in Figure 2.18. In these systems, Ce^4+ salt is reduced by Py and DH˙PDMS and the polymer chains continue to grow as long as Py and Ce^{4+} ion are available. Produced poly(PPy-b-DH˙PDMS) copolymers may be soluble and conductive and have much higher contact angles compared to PPy [19]. The oxidative polymerization of Py with the redox system of Ce^{4+} and DA˙PDMS is carried out in order to produce poly(PPy-b-DA˙PDMS) copolymers and examine the effect of amine functional groups of silicone tegomer on the properties of produced block co-polymers. Increasing DA˙PDMS concentration results in a decrease in the conductivity while an increase occurs in the yield and in the solubility of the copolymers.

The conductivity of the produced copolymer depends on the mol ratio of DA˙PDMS /Py/Ce4+. The copolymers with lower conductivity are soluble in DMF and acetone.The reaction mechanisim can be seen in Figure 2.18.

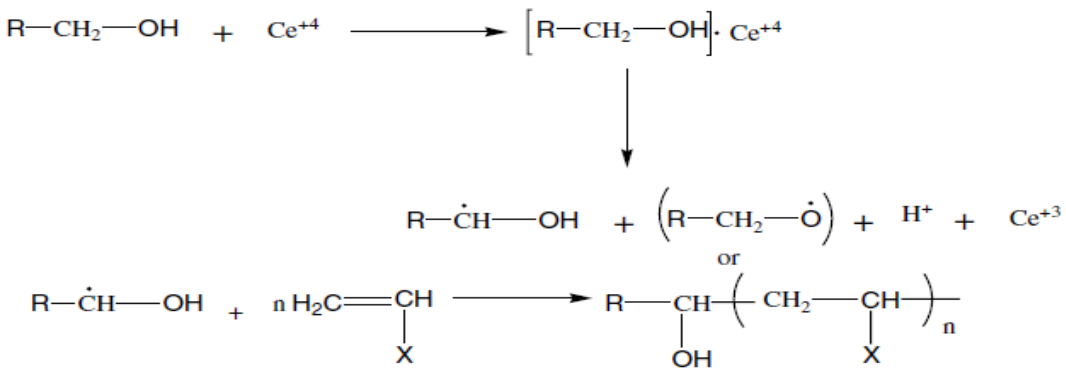


Figure 2.18 : The reaction mechanisim of poly(PPy-b-DA˙PDMS) copolymers.

2.7.3 Pyrrole composites with ceric ion

PPy is a hard, brittle, and nonprocessable solid that is insoluble in common solvents. Neutral polymers are introduced to the polymerization media to overcome the solubility problem of PPy, which is adsorbed in the colloid form onto neutral polymers by the interaction of opposite charges of two macromolecules[89] or by matrix polymerization. [89-91] In the latter case, the polymerization products have low conductivities (10^{-6} S/cm) because of the very low conductivity of the matrix polymer. The other method for improving the mechanical properties of PPy is the preparation of composites from a conducting polymer and an insulating polymer. [92-94] This method improves the mechanical properties of PPy rather than the solubility properties.

The oxidative polymerization of pyrrole (Py) by ceric(IV) ammonium nitrate, in the presence of methyl ethyl ketone/formaldehyde resin was studied and soluble PPy copolymers were produced. These soluble copolymers had conductivity values as high as 10^{-2} S/cm. Ce(IV) salt oxidized both Py and methylol groups of ketonic resins, and block copolymers were formed by the termination reaction of growing PPy radicals with the radicals produced in the ketonic resin by Ce(IV).[1] The polymerization of vinyl mono monomers with a redox initiator system of silicone tegomer and Ce(IV) salt resulted in polymers with silicone tegomer chain ends. [4] Ce(IV) oxidized hydroxymethyl groups of silicone tegomers and yielded radicals that

initiated the polymerization of vinyl monomers.[4] Crosslinked copolymers of Py and silicone compounds were produced electrochemically.[95] However, this method included a number of steps for producing Py-terminated silicone tegomers, and only crosslinked copolymers could be produced. The oxidative polymerization of Py by ceric(IV) ammonium nitrate, in the presence of silicone tegomers with hydroxyl chain ends, was studied with the aim of producing copolymers with higher elasticity, higher solubility, and higher contact angles than PPy. The effect of the concentrations of silicone tegomers, Py, and Ce(IV) on the yield, conductivity, and physical properties of the product was investigated.

Initiation can be shown in Figure 2.19:

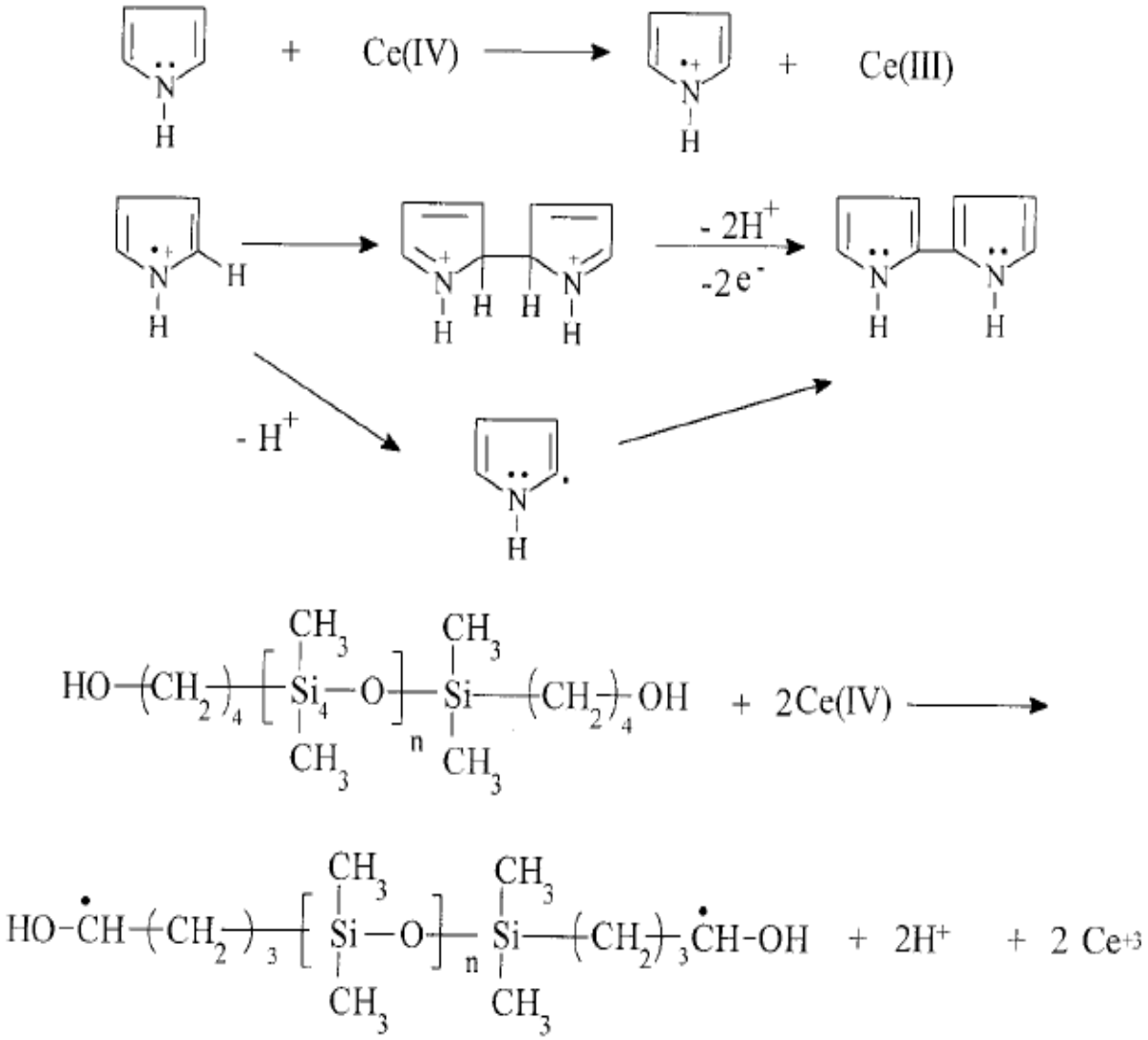


Figure 2.19 : Initiation step of silicone tegomer.

Propagation can be shown in Figure 2.20:

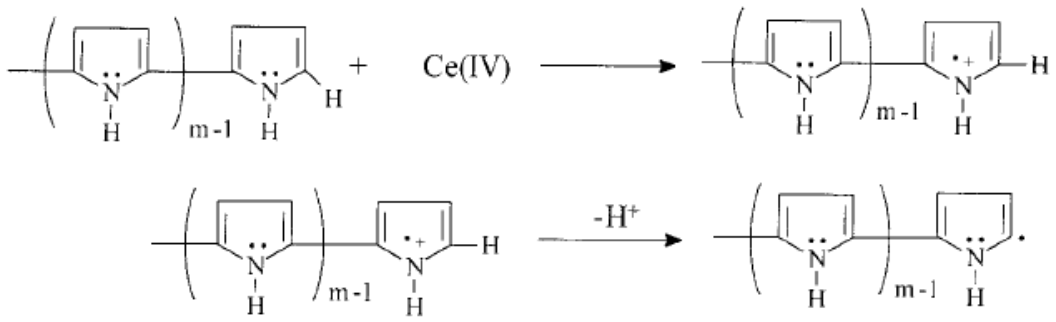


Figure 2.20 : Propagation step of silicone tegomer.

Termination can be shown in Figure 2.21:

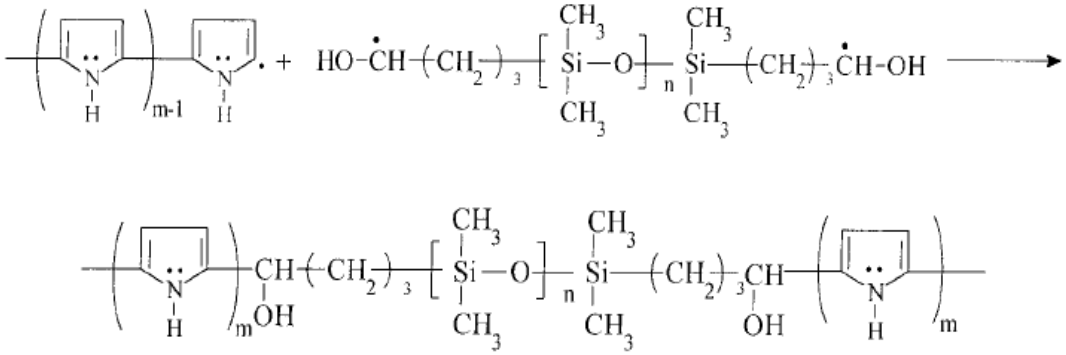


Figure 2.21 : Termination step of silicone tegomer.

PPy/silicone tegomer copolymers were prepared with Ce(IV) as an oxidation agent in a single step. These soluble and conductive copolymers may overcome difficulties in the applications of PPy homopolymers and open new application areas in which the contact angle is also important. Therefore, the copolymers may find a number of new application areas as well as existing PPy applications.

2.8 Pyrrole in Aqueous Media Emulsion Polymerization

Since water is the cheaper and cleaner available solvent, and since in addition the relatively low oxidation potential of pyrrole is compatible with polymerization in aqueous medium, many attempts have been made in this direction, with appreciable success. The main way is the use of surfactants,[96,97] which permits the solubilization of pyrrole in aqueous medium,[98] and therefore its oxidation. In

addition, it allows the use of purely water-soluble oxidants, like permanganate.[99] Emulsion polymerization seems to be the preferred approach, and this approach has continuously drawn researchers' attention until now.[100-101]

However, recently some groups have started to use pure water solutions,adding for example progressively the pyrrole, to minimize the difficulties linked to the relatively low solubility of the monomer[99,102] . This solution can lead to the formation of composites with the second component being the byproduct issued from the oxidant, like a PPy/MnO_2 nanocomposite in the case where $KMnO_4$ is chosen as the oxidant.[99] However, it should be noted that, in comparison with PPy produced in organic medium, the one produced in aqueous solutions or emulsion is always noticeably less conducting, rarely exceeding a few S/cm.

A clever amelioration of the oxidative polymerization method occurred when Miyata and coworkers, mimicking the electrochemical synthesis conditions, had the idea to control the oxidizing power of the oxidant solution by adjusting its redox potential. [103] This was made by adding controlled amounts of the associated reductant (the first example described was adding $FeCl_2$ to a $FeCl_3$oxidant solution). In chemical oxidative polymerization, pyrrole monomers become oxidized by using an oxidizing agent such as ferric chloride, ferric perchlorate and ammonium peroxydisulfate. In the case of PPy sythesis in the form of stable colloids by using polymeric stabilizer or surfactant, the effect of the surfactant molecules is that firstly, they provide requirements for the polymerization reaction to proceed via the emulsion or inverse emulsion pathway. Secondly, they lead to an improvement in properties such as conductivity, stability, solubility in organic solvents, and the processibility.[104] Some advantageous are reported for PPy samples synthesized in the presence of an anionic surfactant.[105] These advantages are mentioned to be improved stability toward deprotonation, better thermooxidative and thermal stability,[105] improved electrical parameters,[104] morphology that is more compact and reduced size PPy globules.[106] Higher solubility is also reported that can be achieved for PPy in the case of using surfactant in the synthesis.[107] It was also reported that the mentioned advantages can be achieved only in the case of using anionic surfactants and cationic or neutral surfactants were reported to be ineffective.[105] So far, the anionic surfactants in the form of free acid or salt have been the mostly used stabilizers for these purposes.[104] Dodecyl benzene sulfonic acid or its substituted derivatives,

sodium dodecyl benzene sulfonate and sodium dodecyl sulfate are among the mostly used surfactants in the form of free acid or salts.

The chemical oxidative polymerization of pyrrole or aniline in aqueous media is a widely used preparative method, mainly for its technical simplicity. The conductivity and other properties of these polymers depend on conditions of their preparation. The nanotubes and nanowires produced by these polymers further stimulated research [108–109]. It has been demonstrated that the acidity of the reaction medium is of crucial importance [108,110] in the development of the polymer morphology and in the understanding of these processes.

Dodecylbenzenesulfonic acid (DBSA) was used for both dopant and emulsifier. The PPy–DBSA sample without clay were synthesized by the emulsion polymerization. Figure 2.22 shows the schematic chemical structures of PPy with interchain links and side chains through two, three coupling mode [111].

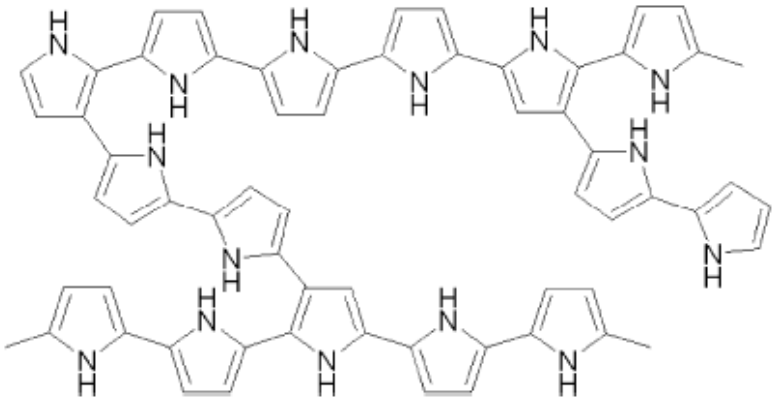


Figure 2.22 : Schematic structure of PPy with interchain links and side chains.

2.9 Nonly Phenol and Etoxylated Nonly Phenol

Chemical structure of ethoxylated nonylphenol can be seen in Figure 2.23.

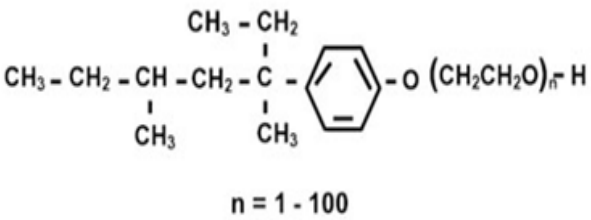


Figure 2.23 : Chemical structure of ethoxylated nonylphenol.

Nonylphenol (NP) is an organic compound of the wider family of alkylphenols. Nonylphenol ethoxylates (ENP) belong to a class of chemicals called alkylphenol ethoxylates. Nonylphenol ethoxylates are liquids or waxy solids depending on the number of ethylene oxide substitutions. NP is a breakdown-product of the non-ionic surfactant ENP. Nonylphenol was first synthesised in 1940 (Soares et all. 2008) and since then, NPs and ENPs have been used in a range of industrial and consumer applications and products. They have recently been used for example in industrial and domestic cleaning chemicals, textile and leather processing, cosmetics, paints, metal cutting, pulp and paper industry, agricultural products and in the plastics industry. Since 2005 the use of NP and ENPs was significantly restricted in the EU in most uses with relevance to waste water emissions.

NP is not very volatile and is unlikely to enter the atmosphere in large amounts. Long-range transboundary air distribution and subsequent atmospheric deposition are also not considered to be an important pathway of NP and ENP . ENPs are more water soluble than NP. Nevertheless, ENP exhibits both hydrophobic and lipophobic properties allowing its use as a surfactant (this being the predominant usage). Nonylphenols are classified as injurious to health, hazardous during consumption, and to have a possible risk of impaired fertility and harm to the unborn child. NP is not a PBT substance (Persistent, Bioaccumulative and Toxic), but it does fulfill the persistence and toxic criteria because it is persistent in the water environment and is classified as very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

Furthermore, nonylphenols are shown to be estrogenic to aquatic organisms. There is quite scarce data on NP and ENP in Baltic Sea marine environment but it seems that NP is found in coastal water and sediments but not in fish . NP is adsorbing strongly to soils and sediments in the environment and to sludge in processes within waste water treatment plants NP is lipophilic, which means that it may bioaccumulate in aquatic organisms, more strongly to mussels than to fish. Even though NP is persistent, it can degrade slowly in the environment inherently biodegradable.

2.9.1 Chemical description of ENP

Nonylphenol (NP) is an organic compound of the wider family alkylphenols, and more specific the group long-chain alkylphenols. The name ‘nonylphenol’ can be

applied to a number of isomer substances having a phenol ring structure and an alkyl chain of C_9H_{19}. Nonylphenols may vary in two ways: the substitution position of the nonyl group on the phenol molecule; and the degree of branching of the nonyl group. The chemical structure of NP is shown in Figure 2.24.

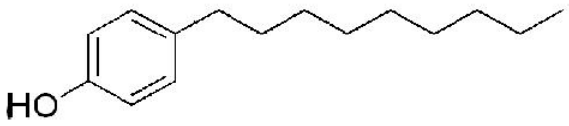


Figure 2.24 : Chemical structure of 4-nonylphenol (straight nonylchain in para position)

Nonylphenol ethoxylates (NPE) belongs to a class of chemicals called alkylphenol ethoxylates. NPE are liquids or waxy solids depending on the number of ethylene oxide substitutions. They are generally colourless to light amber with a varying degree of water solubility. Their physical chemical properties vary with the degree of ethoxylation.

Nonylphenol ethoxylates (NPEs) are nonionic surfactants and are a category of alkylphenol ethoxylates.

Nonylphenol ethoxylates are produced by reacting nonylphenol and ethylene oxide with potassium hydroxide as a catalyst can be seen in Figure 2.25. The ratio of ethylene oxide to nonylphenol determines the molecular weight of the product or the length of the molecule produced. Sometimes water is added to the product to simplify handling.

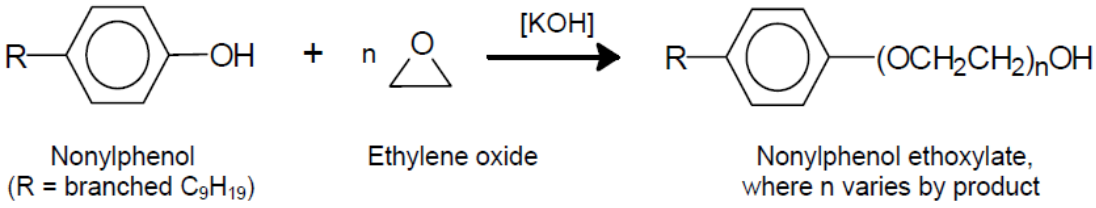


Figure 2.25 : Nonylphenol ethoxylates are produced by reacting nonylphenol and ethylene oxide with potassium hydroxide as a catalyst.

3. EXPERIMENTAL

3.3 Materials

Ceric ammonium nitrate from Analar was dried in oven at 105°C for 1 h and stored in a desiccator. A calculated amount was dissolved in 1M HNO_3 which were purchased from Merck, solution to prepare 0.1M stock solution that was stored in a refrigerator. Ethoxylated nonyl phenols such as nonyl phenol 10 (ENP10), nonyl phenol 30 (ENP30) were commercial grade and supplied by Henkel (Turkey).

3.2 Analyses

FTIR spectra were recorded on a JASCO FTIR 5300 Fourier transform infrared spectrometer using KBr pellets prepared from the copolymers powders.

Electrical conductivities of the solid products were measured by using four point probe technique and WTW micro processor type conductometer.

The polymer pictures were produced by using a Jeol JSM-5410 scanning electron microscope (SEM). The samples were coated with carbon for SEM.

3.3 Conductivity Measurement

To measure electrical conductivity of precipitates, compact thin pellets were prepared under 8-10 tons/cm^2 pressure. A typical sample diameters were 13mm at a thickness of 0.8mm. Conductivity measurements of polymers were performed by the four probe technique and calculated from the following equation (2.1).

$$\sigma = V^{-1} \cdot I(\ln 2 / \pi d_n) \tag{2.1}$$

Parameters are explained individually,where V is the potential (V), I is the current (A), and d_n is the thickness of the samples (cm).

3.4 Preparation of KBR Pellets

If you have dark coloured samples you have to prepare KBr pellet, follow the procedure given below:

The concentration of the sample in KBr should be in the range of 0.2% to 1%. The pellet is much thicker than a liquid film. Too high a concentration usually causes difficulties obtaining clear pellets. The IR beam is absorbed completely, or scattered from the sample which results in very noisy spectra.Although a homogeneous mixture will give the best results, excessive grinding of the potassium bromide is not required. The finely powdered potassium bromide will absorb more humidity (it is hygroscopic) from the air and therefore lead to an increased background in certain ranges. Make sure to work fast. Transfer some KBr out of the oven into a mortar. Add about 1 to 2 % of your sample, mix and grind to a fine powder. For very hard samples, add the sample first, grind, add KBr and then grind again. Lasty They are ready to use in FTIR.

3.5 Preparation of Blank Polypyrrole

The preparation of 0,1 M stok solution of CAN : 100 ml 1 M HNO_3 prepared freshly (7,0 ml HNO_3 dissolve in 100ml water) and used in 50 ml 0,1 M CAN solution (2, 7438 g CAN dissolve in 50 ml nitric acid solution). The reducing compound was dissolved in water. After dissolving the mol ratio of Py /CAN was varied 2,5-5-10-20-50 and Pyrrole monomer added slowly with vigorous stirring to the flask.The molar ratios shown in Table 3.1. The content of the flask was flushed with oxygen-free nitrogen. Cerium ammonium nitrate stock solution was then added drop-wise to the reaction mixture in about 20 min while stirring under room condition at 25°C. The flask is waited for 24 hours on te magnetic stirrer. After 24 hours of polymerization powder was filtered and washed with water and methanol several times and dried at 40 C°.

3.6 Preparation of Polypyrrole and ENP30 Copolymer

The preparetion of 0,1 M stok solution of CAN : 100 ml 1 M HNO_3 prepared freshly (7,0 ml HNO_3 dissolve in 100ml water) and used in 50 ml 0,1 M CAN solution (27438 g CAN dissolve in 50 ml nitric acid solution).

Table 3.1 : The mol ratios and molar concentrations of reaction mixture.

Mol Ratio of Py/CAN	[CAN] mol/L	[Py] mol/L
2,5	0,0640	0,237
5	0,0470	0,237
10	0,0309	0,237
20	0,0183	0,237
50	0,0085	0,237

The reducing compound was dissolved in water. We used 1g ,2 g and 3 g ENP30 and dissolved in 100 ml water. The molar ratios are shown in Table 3.2. After dissolving CAN (91,2 ml) and Pyrrole monomer added (3,2 ml) slowly to the flask with vigorous stirring.The content of the flask was flushed with oxygen-free nitrogen. Cerium ammonium nitrate stock solution was then added drop-wise to the reaction mixture in about 20 min while stirring under room condition at 25°C. The flask waited 24 hours on te magnetic stirrer. After 24 hours of polymerization powder was filtered and washed with water and methanol several times and dried at 40 C°.

Table 3.2 : The mol ratios and molar concentrations of reaction mixture.

[ENP30] mol/L	[CAN] mol/L	[Py] mol/L
0,0033	0,0470	0,237
0,0066	0,0470	0,237
0,0132	0,0470	0,237

The preparetion of 0,1 M stok solution of CAN : 100 ml 1 M HNO_3 prepared freshly (7,0 ml HNO_3 dissolve in 100ml water) and used in 50 ml 0,1 M CAN solution (2, 7438 g CAN dissolve in 50 ml nitric acid solution). The reducing compound was dissolved in water. We used 2 g ENP30 because the most practical values for conductivity and yied is obtained when we use 2 g ENP30 , dissolve 100 ml water. After dissolving the mol ratio of Py /CAN was varied 2,5-5-10-20-50 and Pyrrole monemer added slowly with vigorous stirring to the flask. The molar ratios can be shown in Table 3.3. The content of the flask was flushed with oxygen-free nitrogen. Cerium ammonium nitrate stock solution was then added drop-wise to the reaction mixture in about 20 min while stirring under room condition at 25°C. The flask

waited 24 hours on te magnetic stirrer After 24 hours of polymerization powder. was filtered and washed with water and methanol several times and dried at 40 C°.

Table 3.3: The mol ratios and molar concentrations of reaction mixture.

Mol Ratio of Py/CAN	[CAN] mol/L	[Py] mol/L	[ENP30] mol/L
2,5	0,0640	0,237	0,0066
5	0,0470	0,237	0,0066
10	0,0309	0,237	0,0066
20	0,0183	0,237	0,0066
50	0,0085	0,237	0,0066

3.7 Preparation of Polypyrrole and ENP10 Cpolymer

The preparetion of 0,1 M stok solution of CAN : 100 ml 1 M HNO_3 prepared freshly (7,0 ml HNO_3 dissolve in 100ml water) and used in 50 ml 0,1 M CAN solution (2, 7438 g CAN dissolve in 50 ml nitric acid solution). The reducing compound was dissolved in water. We used 1g,2 g and 3g NP10 Etoxylated and dissolve 100 ml water. The molar ratios are shown in Table 3.4. After dissolving CAN (91,2 ml) and Pyrrole monomer added (3,2 ml) slowly with vigorous stirring to the flask.The content of the flask was flushed with oxygen-free nitrogen. Cerium ammonium nitrate stock solution was then added drop-wise to the reaction mixture in about 20 min while stirring under room condition at 25°C. The flask waited 24 hours on te magnetic stirrer. After 24 hours of polymerization powder was filtered and washed with water and methanol several times and dried at 40 C°.

Table 3.4: The mol ratio and molar concentration of reaction mixture.

[ENP10] mol/L	[CAN] mol/L	[Py] mol/L
0,0077	0,0470	0,237
0,0154	0,0470	0,237
0,0308	0,0470	0,237

The preparetion of 0,1 M stok solution of CAN : 100 ml 1 M HNO_3 prepared freshly (7,0 ml HNO_3 dissolve in 100ml water) and used in 50 ml 0,1 M CAN solution (2, 7438 g CAN dissolve in 50 ml nitric acid solution) The reducing compound was dissolved in water. We used 2 g ENP10 because the most practical values for

conductivity and yied is obtained when we use 2 g ENP10 and dissolve 100 ml water. After dissolving the mol ratio of Py /CAN was varied 2,5-5-10-20-50 and Pyrrole monemer added slowly with vigorous stirring to the flask. The molar ratios are shown in Table 3.5. The content of the flask was flushed with oxygen-free nitrogen. Cerium ammonium nitrate stock solution was then added drop-wise to the reaction mixture in about 20 min while stirring under room condition at 25°C. The flask waited 24 hours on te magnetic stirrer. After 24 hours of polymerization powder was filtered and washed with water and methanol several times and dried at 40 C°.

Table 3.5: The mol ratio and molar concentration of reaction mixture.

Mol Ratio of Py/CAN	**[CAN] mol/L**	**[Py] mol/L**	**[ENP10] mol/L**
2,5	0,0640	0,237	0,0154
5	0,0470	0,237	0,0154
10	0,0309	0,237	0,0154
20	0,0183	0,237	0,0154
50	0,0085	0,237	0,0154

4. RESULT AND DISCUSSIONS

The conductivities and solubilities and yields of the various pyrrole substituted copolymers at room temperature are listed in Tables which are below. The tables which include the effect of Ce^{+4} salt and the pyrrole on yield, solubility and conductivity was investigated as well as ENP type. The resulting copolymers were characterized by spectroscopic method.

4.1 Blank Polypyrrole

The initial step in the chemical polymerization of Py is thought to be the formation of Py radical cations. The oxidation of Py by Ce(IV) forms radical cations (Py^{+}), which can dimerize with the expulsion of $2H^{+}$ in the proposed mechanism for chemical synthesis of blank Ppy. The second mechanistic possibility in the initiation step is the proton loss of radical cations to form Py radicals, which dimerize. In the propagation step, the polymer chains continue to grow as long as Py and Ce(IV) are available. In the termination step, the growing PPy chains may combine with other PPy chains to produce PPy. Conductivities solubilities and yields of blank polypyrrole can be seen in Table 4.1.

Initiation step can be shown in Figure 4.1.

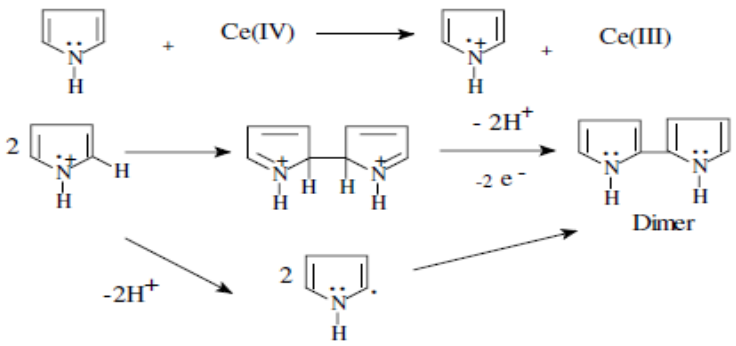


Figure 4.1: The initiation reaction of Ppy.

Propagation/Termination step can be shown in Figure 4.2.

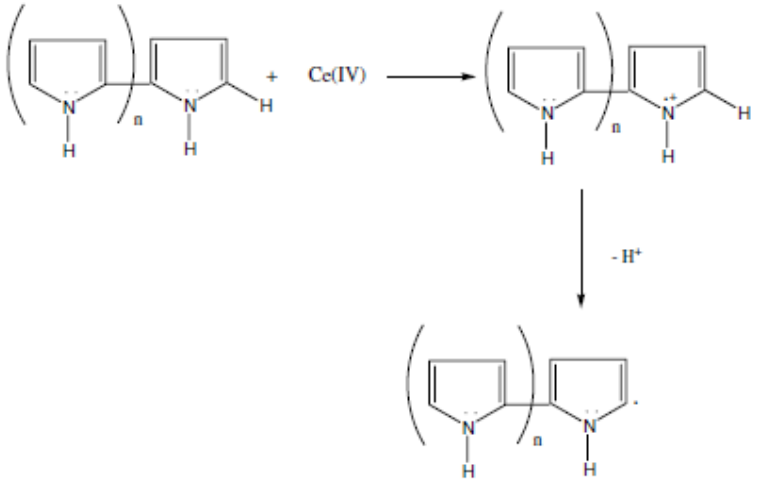


Figure 4.2: The propagation/termination reaction of Ppy.

Table 4.1 : Conductivities solubilities and yields of blank polypyrrole.

Sample Name	Mol Ratio of Py/CAN	[CAN] mol/L	Yield (g)	Conductivity (S/cm)	Solubility		
					Acetone	DEMSO	DMF
PPy-1	2,5	0,0640	0,8208	$1,7x10^{-2}$	insoluble	slightly soluble	insoluble
PPy-2	5	0,0470	1,533	$2,2x10^{-2}$	insoluble	slightly soluble	insoluble
PPy-3	10	0,0309	2,182	$9,8x10^{-3}$	insoluble	slightly soluble	insoluble
PPy-4	20	0,0183	0,247	$3,4x10^{-3}$	insoluble	slightly soluble	insoluble
PPy-5	50	0,0085	0,0283	$1,6x10^{-3}$	insoluble	slightly soluble	insoluble

[Py]: 0,237 mol/L T:25 ˚C t:24h

The effect of concentration on the conductivity was examined for different concentration of CAN. It is seen that , the conductivities increases with respect to the CAN concentration, of cource this result is expectable. The concentration of Ce salt varied between 0,064 mol/L and 0,0085 mol/L keeping the other parameters of polymerization constant. An increase in the ceric ion concentration caused the polymerization yield to increase. The limiting conversation reached a maximum value when ceric ion concentration was 0,0309 mol/L can be shown in Figure 4.3.

Increasing the Ce^{+4} concentration above this value resulted in the yield of polymerization to become inversely proportional to Ce^{+4} concentration, probably because of linear termination by Ce^{+4}. Besides, increasing Ce^{+4} concentration is known to cause a significant increase in the rate of oxidative termination of primary radicals compared with the rate of initiation. Oxidative chain termination and linear termination by Ce^{+4} ions probably was significant at higher Ce^{+4} concentration (0,0470 mol/L) conductivity became inversely proportional to the Ce^{+4} concentration.

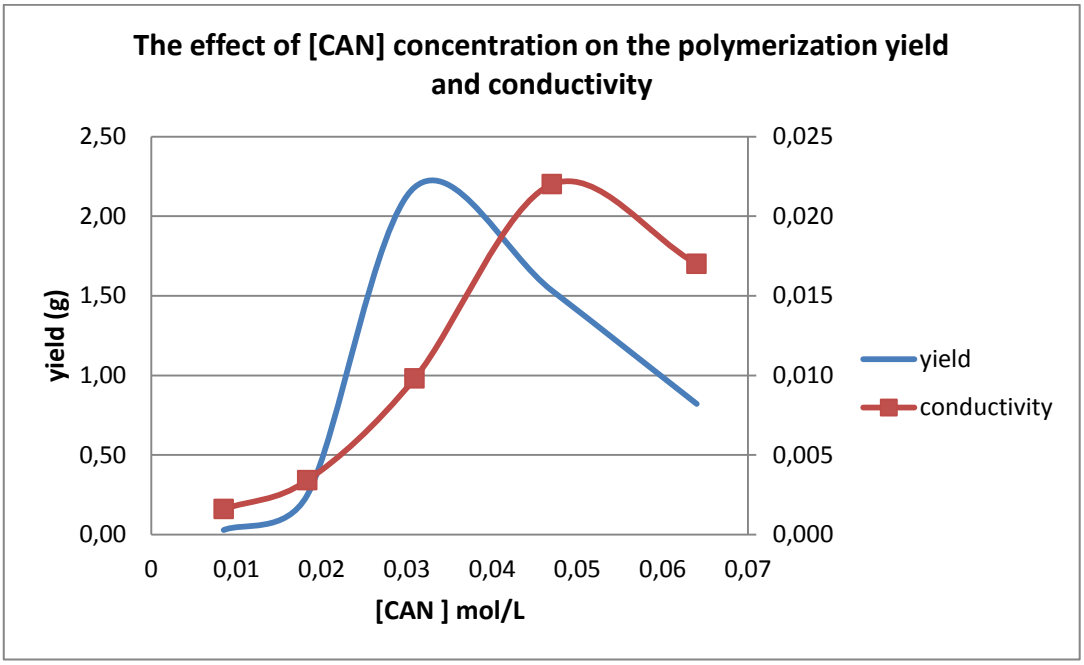


Figure 4.3 : The effect of [CAN] concentration on the polymerization yield and conductivity. [Py]: 0,237 mol/.

Figure 4.4, Figure 4.5, Figure 4.6, Figure 4.7 and Figure 4.8, show the FTIR spectra of blank PPy. For Figure 4.6 the peaks at 783 cm^{-1}, 933 cm^{-1} are attributed to C–H wag- ging attributed to C–H wagging, peak at 1040 cm^{-1} indicative of =C H in plane deformation vibration, peak at 1115 cm^{-1} attributed to C-H in and out of plane deformations, peak at 1211 cm^{-1} attributed to N–C stretching band . The characteristic peaks at 1553 cm^{-1} and 1484 cm^{-1} correspond to the C=C stretching, whereas peaks at 1674 cm^{-1} and 1305 cm^{-1} represent to re- spectively, C=N and C–N bonds . The occurrence of small peaks at 3273 cm^{-1} is assigned to presence of N–H stretching vibrations. The peak at 2895 cm^{-1} was the result of aliphatic C-H vibration. The peak at 1384 cm^{-1} was due to a NO_3^- ligand incorporated into the polymer. This peak was always observed as a sharp band in the spectrum of the copolymer. It is

result of high oxidation.The peaks observed in the present work match well with the ones available in the literature confirming the formation of Polypyrrole.

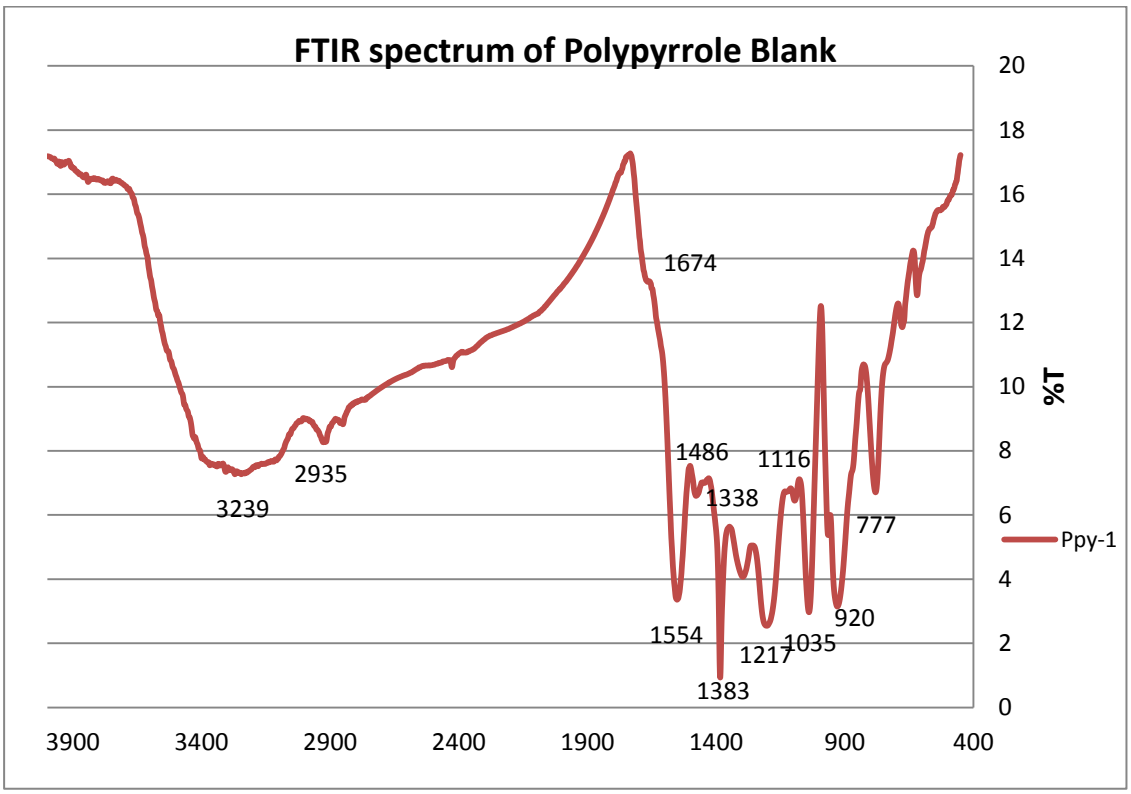


Figure 4.4 : FTIR spectrum of Polypyrrole Blank (PPy-1).

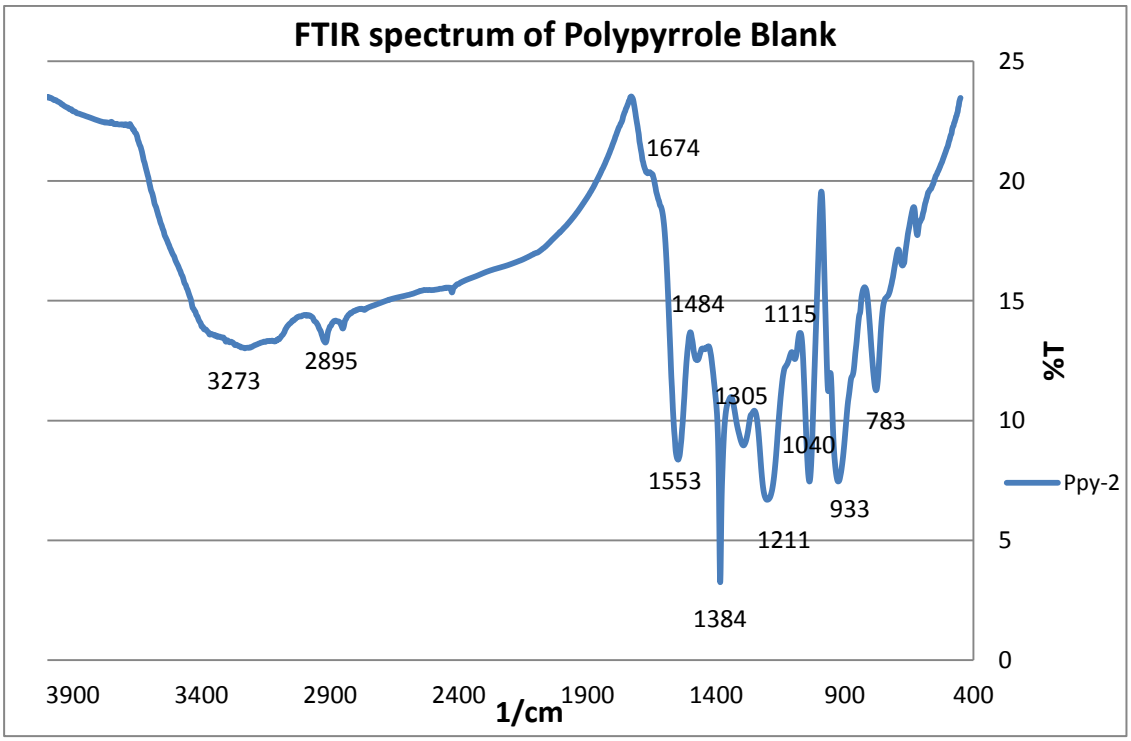


Figure 4.5 : FTIR spectrum of Polypyrrole Blank (PPy-2).

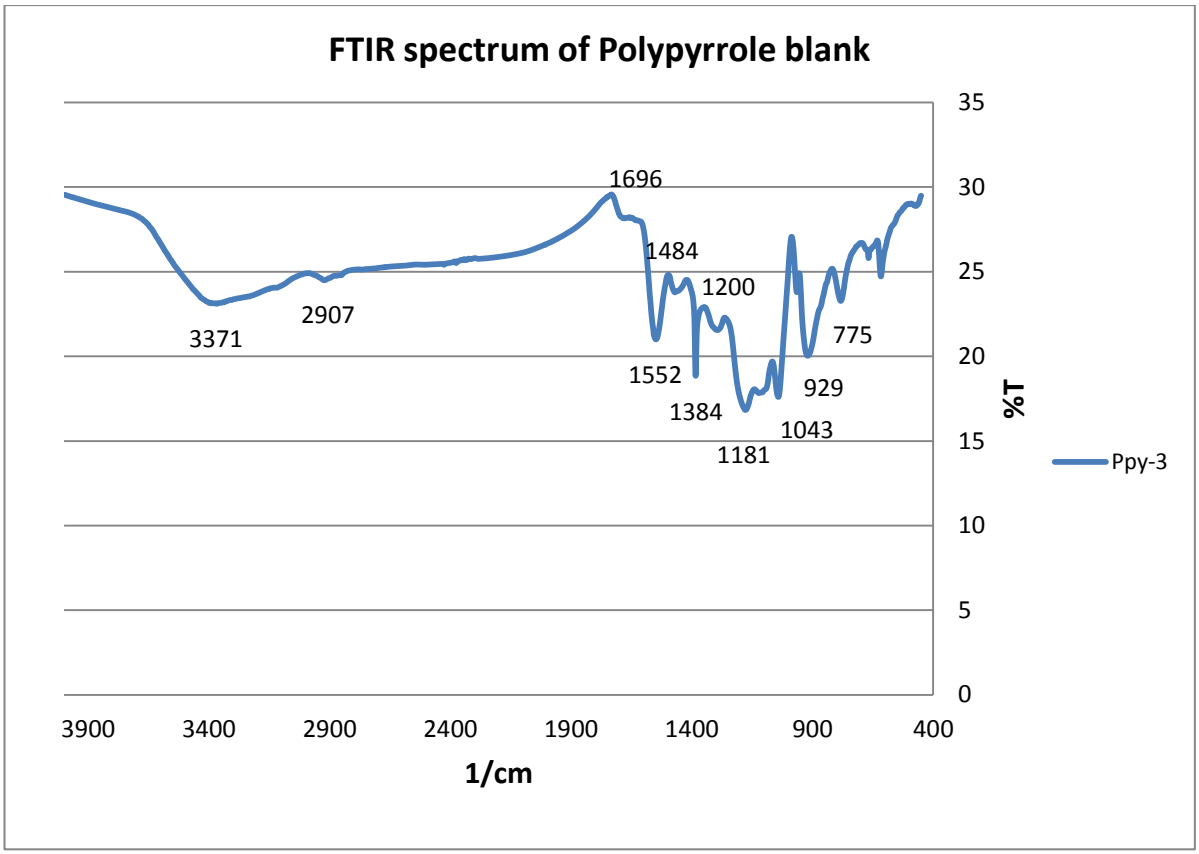


Figure 4.6 : FTIR spectrum of Polypyrrole Blank (PPy-3).

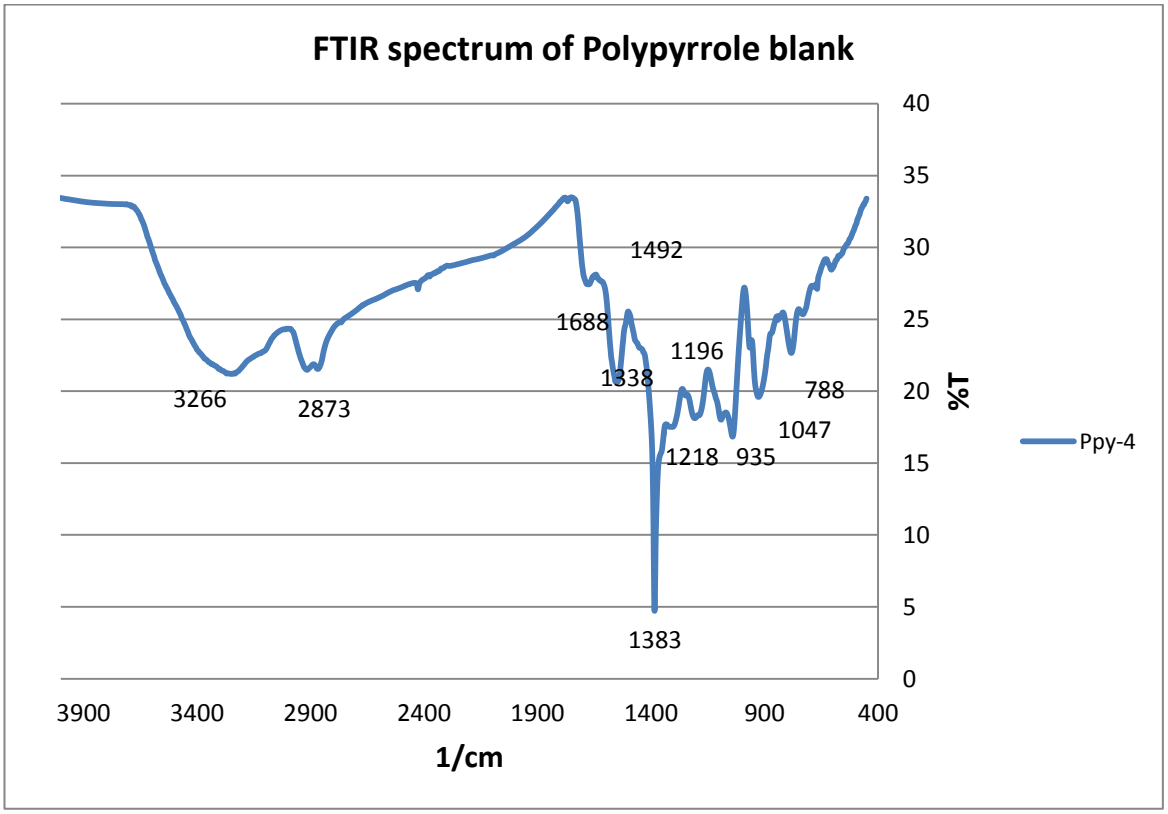


Figure 4.7 : FTIR spectrum of Polypyrrole Blank (PPy-4).

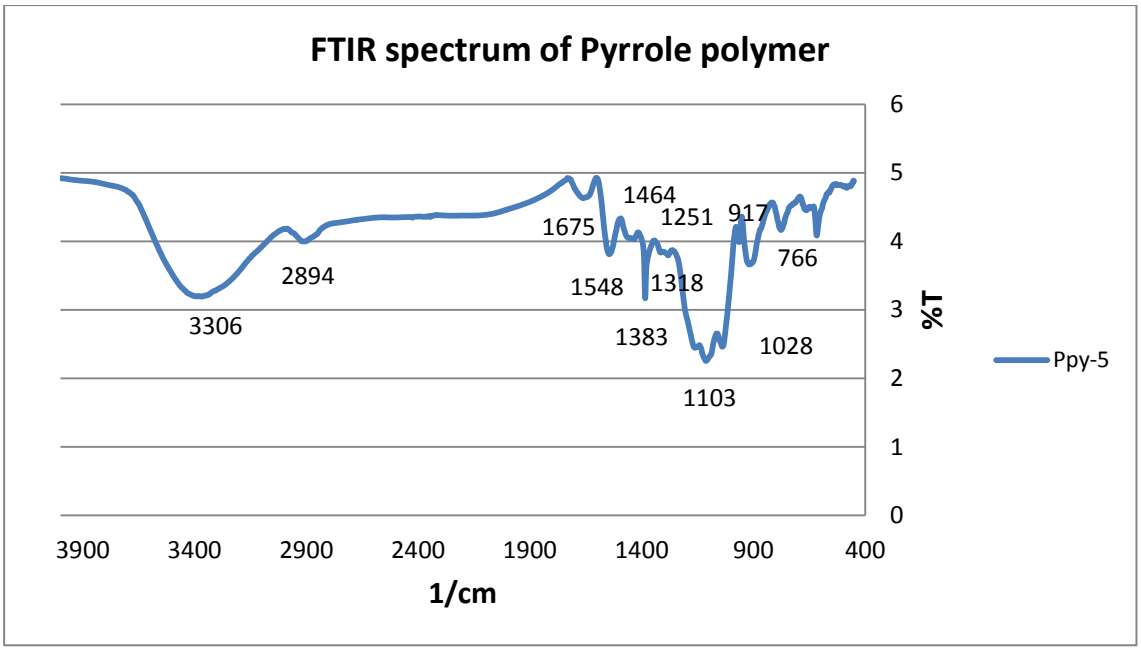


Figure 4.8 : FTIR spectrum of Polypyrrole Blank (Ppy-5).

The scanning elecron microscope sample pictures shows us that we obtain nano scale PPy particles can be seen in Figure 4.9 and Figure 4.10.

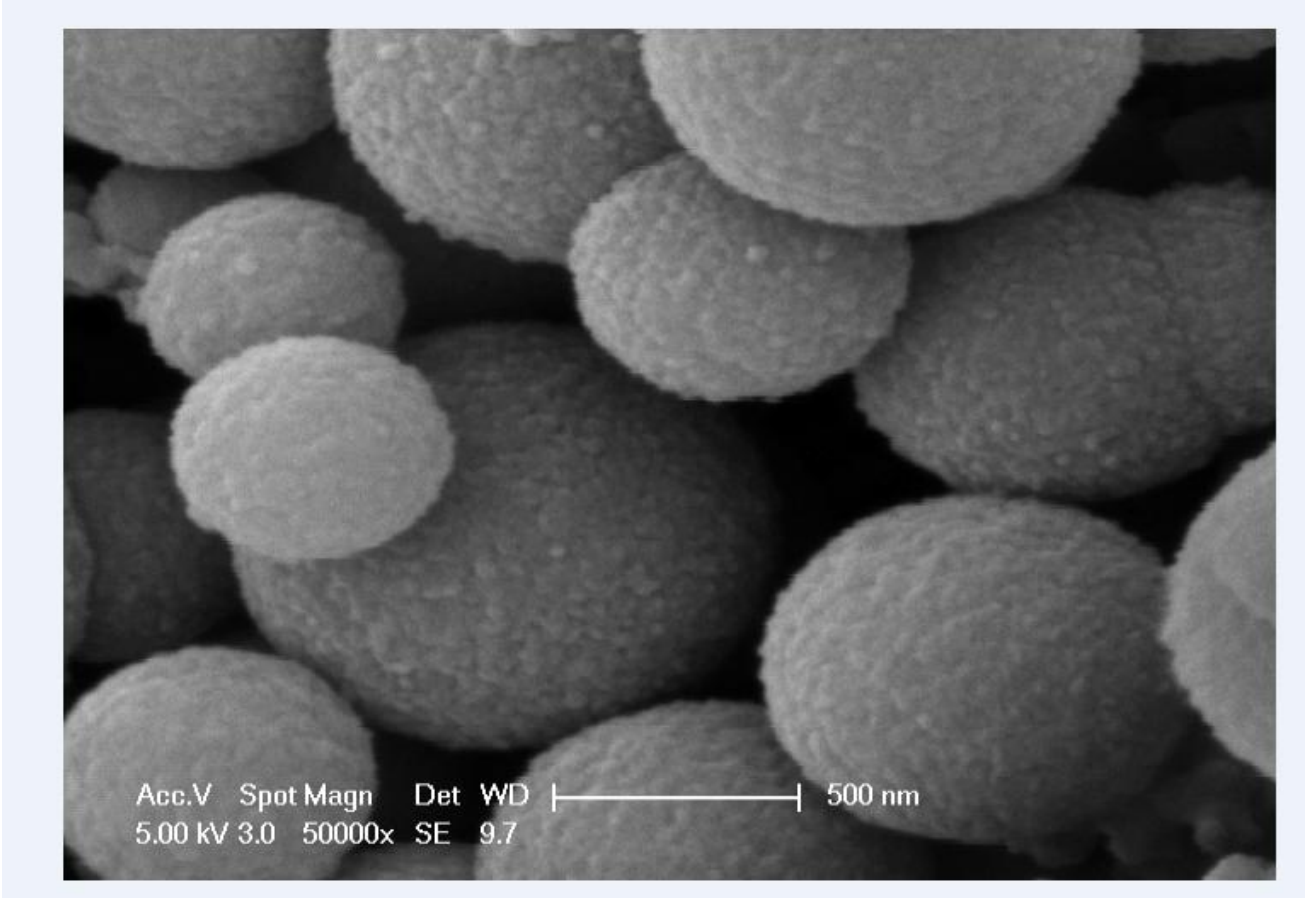


Figure 4.9 : The SEM picture of Polypyrrole Blank (Ppy-2) in 500 nm.

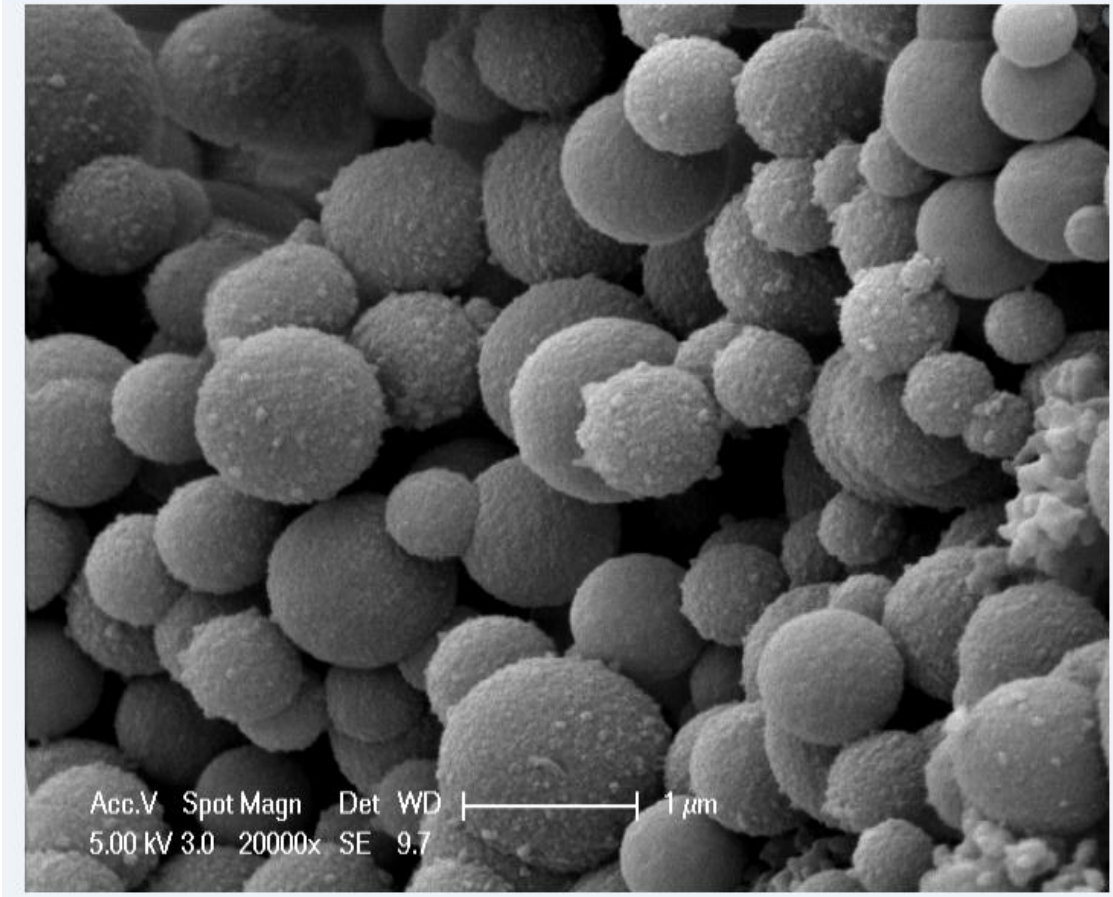


Figure 4.10 : The SEM picture of Polypyrrole Blank (Ppy- 2) in1 μm.

4.2 ENP30 and Polypyrrole Copolymer

The initial step in the chemical polymerization of Py is thought to be the formation of Py radical cations can be seen in Figure 4.11. The oxidation of Py by Ce(IV) forms radical cations (Py^+), which can dimerize with the expulsion of $2H^+$ in the proposed mechanism for chemical synthesis of Ppy and ENP 30 copolymer. The second mechanistic possibility in the initiation step is the proton loss of radical cations to form Py radicals, which dimerize. Ce(IV)/ethylol redox reaction also occurs, and free radicals are generated in the initiation step.In the propagation step, the polymer chains continue to grow as long as Py and Ce(IV) are available. In the termination step, the growing PPy chains may combine with with ENP30 radicals to produce PPy-b-ENP30 copolymers. Conductivities solubilities and yields of ENP30 and PolyPyrrole Copolymer can be shown in Table 4.2. The effect of [CAN] concentration on polymerization yield and conductivity of Polypyrrole and ENP30 copolymer display in Table 4.3.

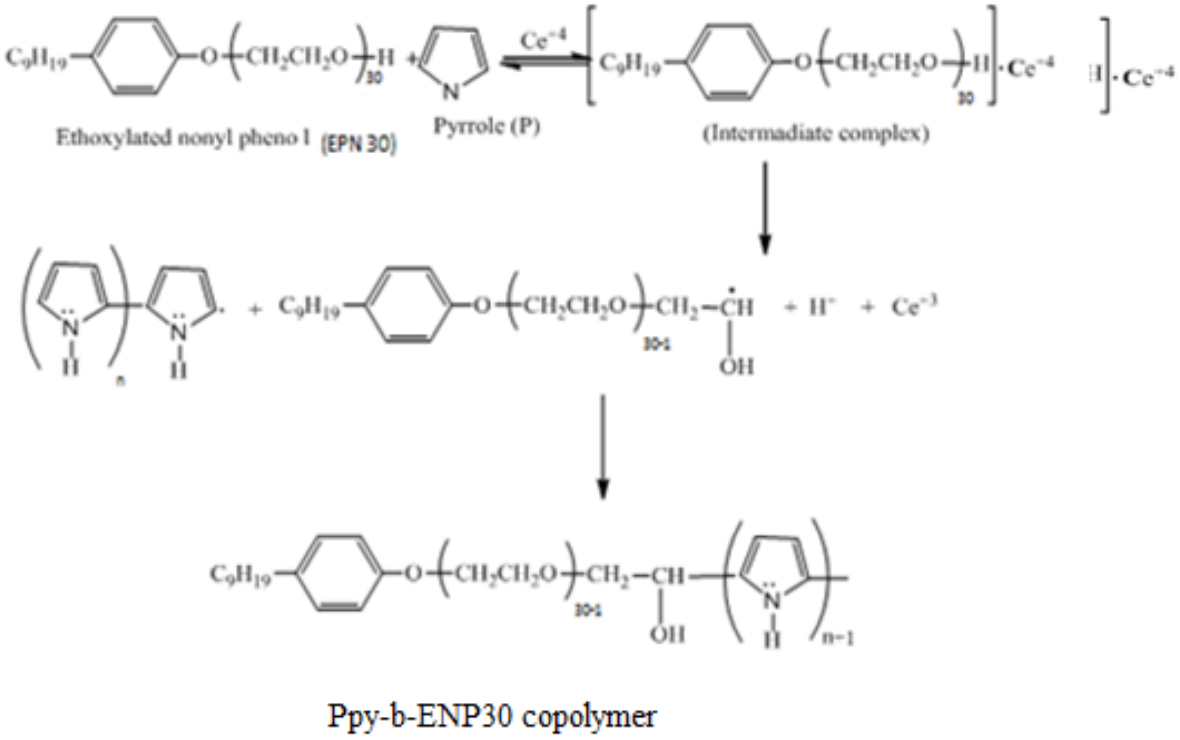


Figure 4.11 : The formation reaction of PolyPyrrole and ENP30 copolymer.

Table 4.2 : Conductivities solubilities and yields of ENP30 and PolyPyrrole Copolymer.

Sample Name	[ENP30] mol/L	Yield (g)	Conductivity (S/cm)	Solubility		
				Acetone	DMSO	DMF
PPy-b-ENP30-1	0,0033	0,454	$5,3x10^{-3}$	insoluble	slightly soluble	insoluble
PPy-b-ENP30-2	0,0066	0,640	$1,1x10^{-2}$	insoluble	slightly soluble	insoluble
PPy-b-ENP30-3	0,0132	0,560	$2,1x10^{-3}$	insoluble	slightly soluble	insoluble

[CAN]:0,047 mol/L, [Py]:0,237 mol/L T:25 ˚C t:24 h

The effect of reducing agent concentration on the yield of polymerization is shown in Figure 4.12. The polymerization yield reached the high value when ethoxylated nonyl phenol concentration was about 20 g/L. A further increase in ethoxylated nonyl phenol (ENP30) caused degradative chain transfer reaction to become significant compared with bimolecular termination, so the yield decreased with increasing ENP30 concentration about 20 g/L.

we see that the conductvities of these copolymers are not high enough,if it is compared with polypyrrole. The water-soluble of nonylphenolethoxylates diminishes the conductivity of copolymer becaue of its surfactant structure.

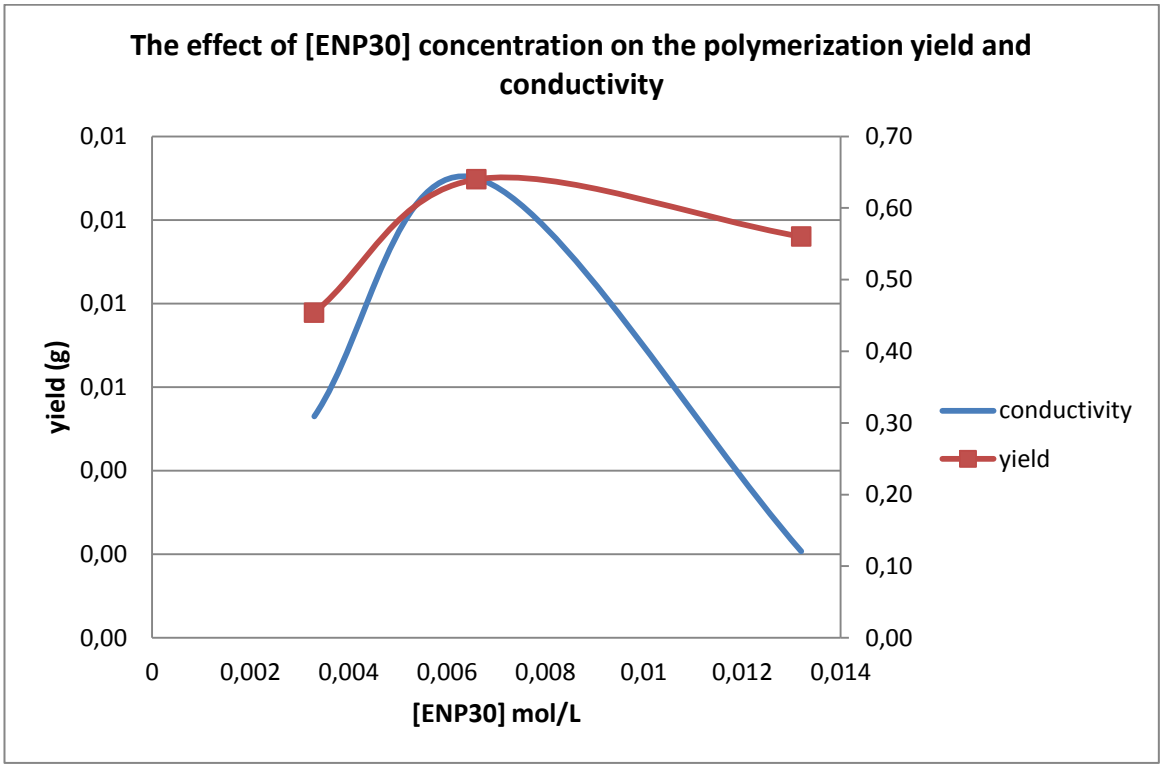


Figure 4.12 : The effect of ENP30 concentration on polymerization yield and conductivity [CAN]:0,047 mol/L [Py]:0,237 mol/L.

Figure 4.13 shows the FTIR spectra of PPy-b-ENP30. The peaks at 795 cm^{-1}, 943 cm^{-1} are attributed to C–H wag- ging attributed to C–H wagging, peak at 1049 cm^{-1} indicative of =C H in plane deformation vibration, peak at 1101 cm^{-1} attributed to C-H in and out of plane deformations. The characteristic peaks at 1552 cm^{-1} and 1474 cm^{-1} correspond to the C=C stretching, whereas peaks at 1662 cm^{-1} and 1303 cm^{-1} represent to re- spectively, C=N and C–N bonds . The occurrence of small peaks at 428 cm^{-1} is assigned to presence of N–H stretching vibrations. The peak at 2895 cm^{-1} was the result of aliphatic C-H vibration. The peak at 1384 cm^{-1} was due to a NO_3^- ligand incorporated into the polymer. This peak was always observed as a sharp band in the spectrum of the copolymer. For ENP30 the spectrum with peaks etoksi (CH_3CH_2-O-) C-H stretching at 2925 cm^{-1} and C-O stretching peaks at 1175 cm^{-1}.

The effect of concentration on the conductivity was examined for different concentration of CAN of Polypyrrole and ENP30 copolymer. The concentration of Ce salt varied between 0,064 mol/L and 0,0085 mol/L keeping the other parameters

of polymerization constant. An increase in the ceric ion concentration caused the polymerization yield to increase.

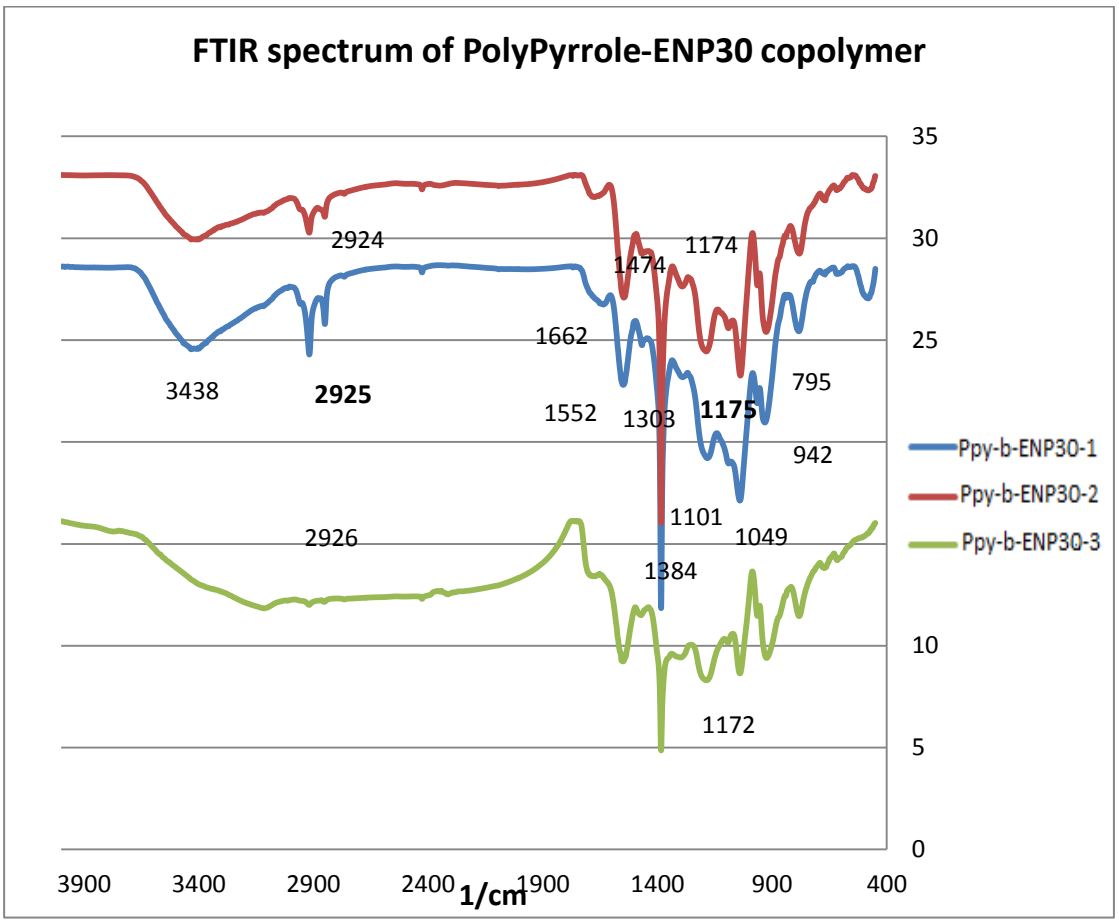


Figure 4.13 : FTIR spectrum of PolyPyrrole and ENP30 Copolymer.

Table 4.3 : The effect of [CAN] concentration on polymerization yield and conductivity of Polypyrrole and ENP30 copolymer.

Sample Name	Mol Ratio of Py/CAN	[CAN] mol/L	Yield(g)	Conductivity S/cm
PPy-b-ENP30-4	2,5	0,0640	0,413	$4,6x10^{-3}$
PPy-b-ENP30-2	5	0,0470	0,604	$1,1x10^{-2}$
PPy-b-ENP30-5	10	0,0309	0,249	$0,6x10^{-3}$
PPy-b-ENP30-6	20	0,0183	0,0907	$5,3x10^{-4}$
PPy-b-ENP30-7	50	0,0085	0,0257	$1,1x10^{-4}$

[ENP30]:0,0066 mol/L; [Py]: 0,237 mol/L T:25 ˚C T:24 h

The limiting conversation reached a maximum value when ceric ion concentration was 0,0470 mol/L can be shown in Figure 4.14. Increasing the Ce^{+4} concentration

above this value resulted in the yield of polymerization to become inversely proportional to Ce^{+4} concentration, probably because of linear termination by Ce^{+4}. Besides, increasing Ce^{+4} concentration is known to cause a significant increase in the rate of oxidative termination of primary radicals compared with the rate of initiation. Oxidative chain termination and linear termination by Ce^{+4} ions probably was significant at higher Ce^{+4} concentration (0,0470 mol/L) conductivity became inversely proportional to the Ce^{+4} concentration. We see that the conductvities of these copolymers are not high enough,if it is compared with polypyrrole. The water-soluble of nonylphenolethoxylates diminishes the conductivity of copolymer becaue of its surfactant structure.

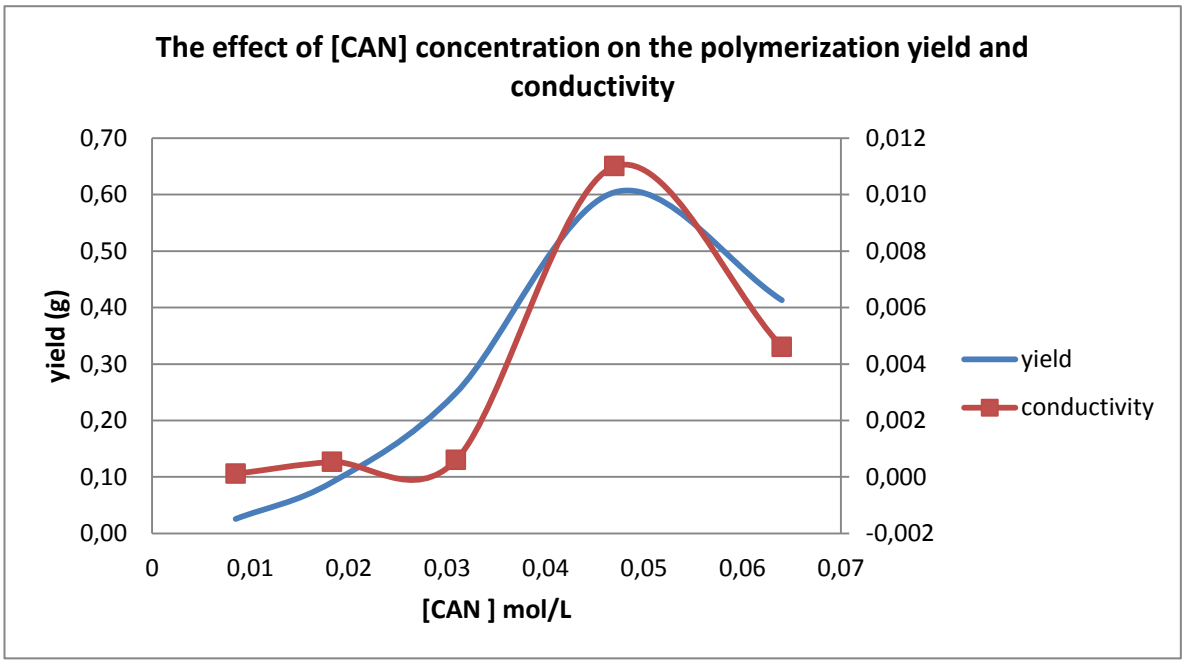


Figure 4.14 : The effect of [CAN] concentration on the polymerization yield and conductivity. [Py]: 0,237 mol/L [ENP30]:0,0066 mol/L.

Figure 4.15 shows the FTIR spectra of PPy-b-ENP30 The peaks at 781 cm^{-1}, 940 cm^{-1} are attributed to C–H wag- ging attributed to C–H wagging, peak at 1042 cm^{-1} indicative of =C H in plane deformation vibration, peak at 1221 cm^{-1} attributed to N–C stretching band . The characteristic peaks at 1554 cm^{-1} and 1482 cm^{-1} correspond to the C=C stretching, whereas peaks at 1675 cm^{-1} and 1311 cm^{-1} represent to re-spectively, C=N and C–N bonds . The occurrence of small peaks at 3274 cm^{-1} is assigned to presence of N–H stretching vibrations. The peak at 1384 cm^{-1} was due to a NO_3^- ligand incorporated into the polymer. This peak was always observed as a

sharp band in the spectrum of the copolymer. For NPE30 the spectrum with peaks etoksi (CH_3CH_2-O-) C-H stretching at 2905 cm^{-1} and C-O stretching peaks at 1170 cm^{-1}.

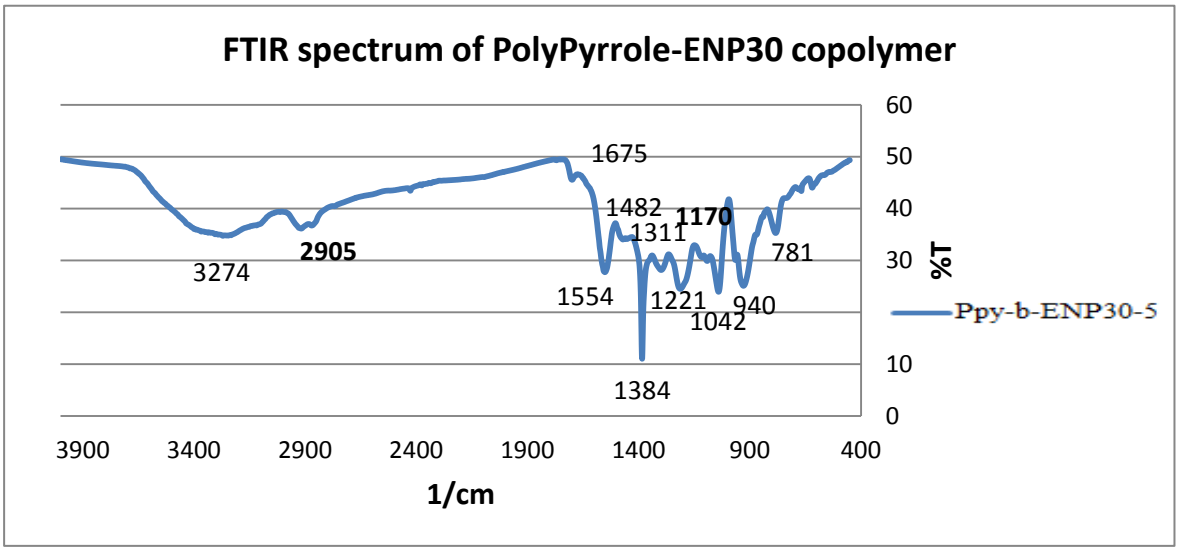


Figure 4.15 :FTIR spectrum of PolyPyrrole and ENP30 Copolymer(Ppy-b-NPE30-5).

The scanning elecron microscope sample pictures shows us that we obtain nano scale PolyPyrrole and ENP30 Copolymer particles can be seen in Figure 4.16.

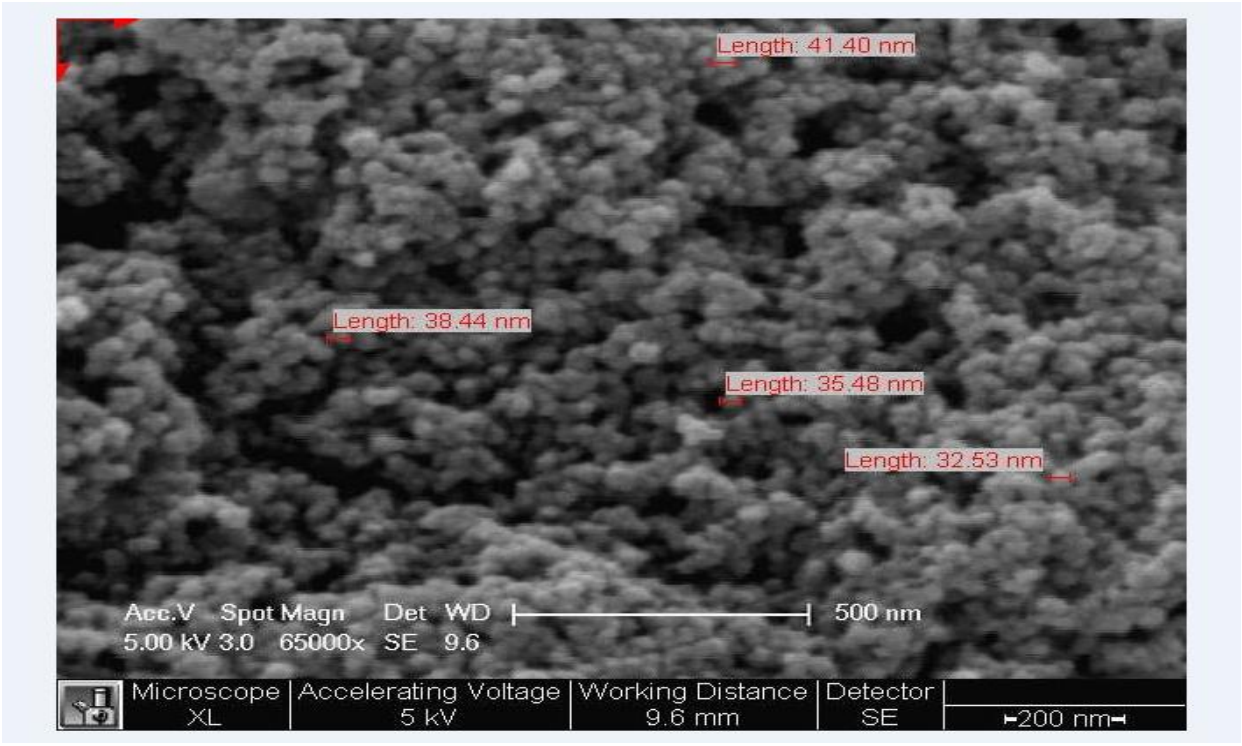


Figure 4.16 : The SEM picture of PolyPyrrole and ENP30 Copolymer PPy-b-ENP30-2 in 200 nm.

4.3 ENP10 and Polypyrrole Copolymer

The initial step in the chemical polymerization of Py is thought to be the formation of Py radical cations can be shown in Figure 4.17. The oxidation of Py by Ce(IV) forms radical cations (Py^{+}), which can dimerize with the expulsion of $2H^{+}$ in the proposed mechanism for chemical synthesis of Ppy and ENP10 copolymer. The second mechanistic possibility in the initiation step is the proton loss of radical cations to form Py radicals, which dimerize. Ce(IV)/ethylol redox reaction also occurs, and free radicals are generated in the initiation step.In the propagation step, the polymer chains continue to grow as long as Py and Ce(IV) are available. In the termination step, the growing PPy chains may combine with with NPE10 radicals to produce PPy-b-ENP10 copolymers can be shown in Figure 4.17. Conductivities solubilities and yields of Polypyrrole and ENP10 can be seen in Table 4.4. The effect of [CAN] concentration on polymerization yield and conductivity of PolyPyrrole and ENP10 copolymer can be seen in Table 4.5.

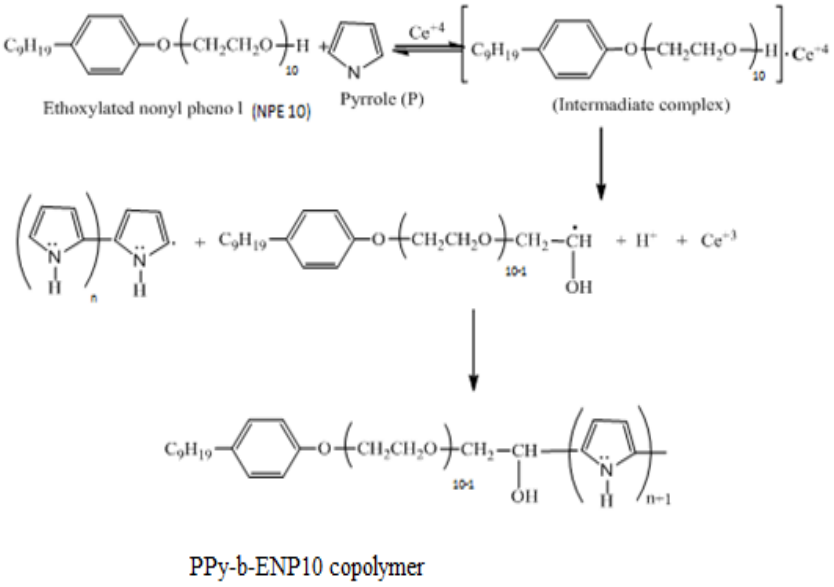


Figure 4.17 : The formation reaction of PolyPyrrole and ENP10 copolymer.

The effect of reducing agent concentration on the yield of polymerization is shown in Figure 4.18. The polymerization yield reached The high value when ethoxylated nonyl phenol concentration was about 20 g/L. A further increase in ethoxylated nonyl phenol (ENP10) caused degradative chain transfer reaction to become

significant compared with bimolecular termination, so the yield decreased with increasing ENP10 concentration about 20 g/L.

Table 4.4 : Conductivities solubilities and yields of Polypyrrole and ENP10 Copolymer.

Sample Name	[ENP10]	Yield (g)	Conductivity (S/cm)	Solubility		
				Acetone	DMSO	DMF
PPy-b-NPE10-1	0,0077	0,478	0,00408	soluble	slightly soluble	insoluble
PPy-b-NPE10-2	0,0154	0,604	0,0122	soluble	slightly soluble	insoluble
PPy-b-NPE10-3	0,0308	0,522	0,00204	soluble	slightly soluble	insoluble

[CAN]:0,047mol/L [Py]:0,237 mol/L T:25 ˚C t:24 h

we see that the conductvities of these copolymers are not high enough,if it is compared with polypyrrole. The water-soluble of nonylphenolethoxylates diminishes the conductivity of copolymer becaue of its surfactant structure. The yield incease by increased [CAN] concentrations, respectively.

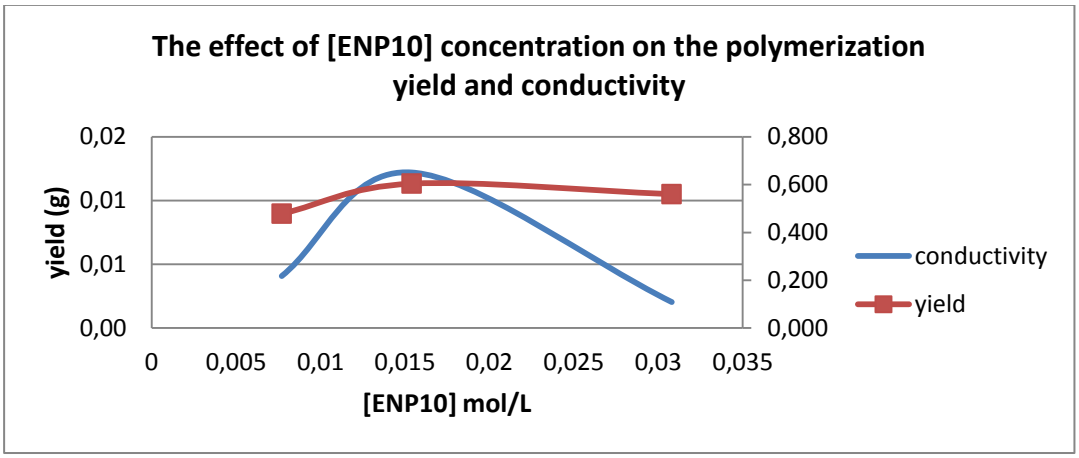


Figure 4.18 : The effect of ENP10 concentration on polymerization yield and conductivity [CAN]:0,047mol/L, [Py]:0,237mol/L.

Figure 4.19 shows the FTIR spectra of PPy-b-ENP10 copolymer The peaks at 781 cm^{-1}, 938 cm^{-1} are attributed to C–H wag- ging attributed to C–H wagging, peak at 1041 cm^{-1} indicative of =C H in plane deformation vibration, peak at 1109 cm^{-1} attributed to C-H in and out of plane deformations. The peak at 1208 cm^{-1} attributed to N–C stretching band . The characteristic peaks at 1559 cm^{-1} and 1474 cm^{-1}

correspond to the C=C stretching, whereas peak at 1694 cm^{-1} C=N and C–N bonds . The occurrence of small peaks at 3261 cm^{-1} is assigned to presence of N–H stretching vibrations. The peak at 1384 cm^{-1} was due to a NO_3^- ligand incorporated into the polymer. This peak was always observed as a sharp band in the spectrum of the copolymer. For ENP10 the spectrum with peaks etoksi (CH_3CH_2-O-) C-H stretching at 2915 cm^{-1} and C-O stretching peaks at 1185 cm^{-1}.

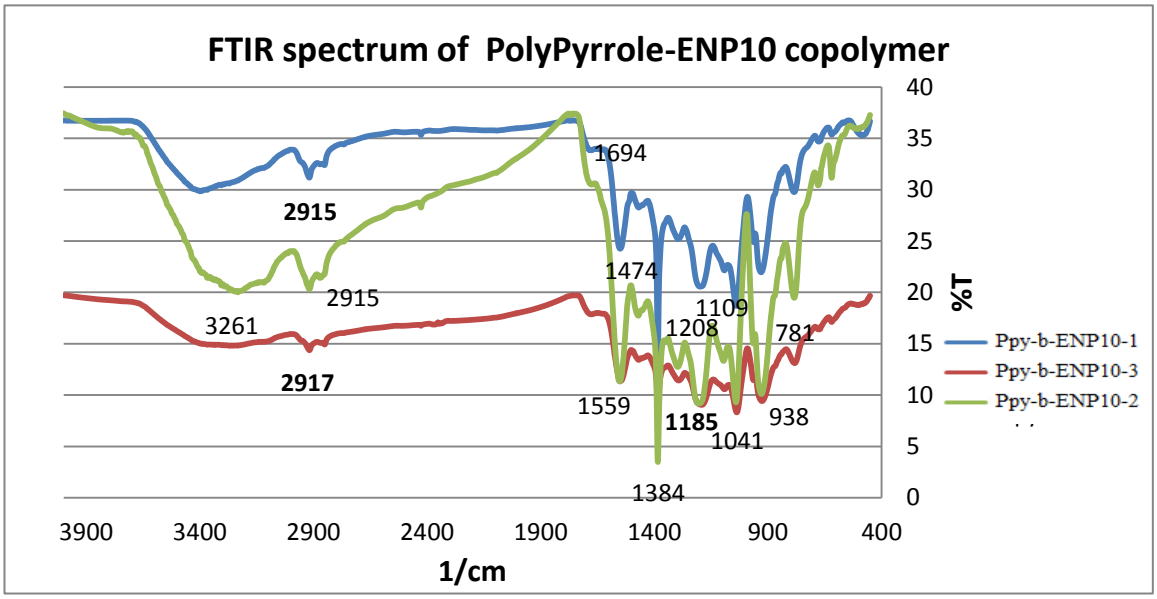


Figure 4.19 : FTIR spectrum of PolyPyrrole and ENP10 Copolymer**.**

Table 4.5: The effect of [CAN] concentration on polymerization yield and conductivity of PolyPyrrole and ENP10 copolymer.

Sample Name	Mol Ratio of Py/CAN	[CAN] mol/L	Yield(g)	Conductivity S/cm
PPy-b-ENP10-4	2,5	0,0640	0,413	$5,4x10^{-3}$
PPy-b-ENP10-2	5	0,0470	0,604	$1,2x10^{-2}$
PPy-b-ENP10-5	10	0,0309	0,249	$9,3x10^{-3}$
PPy-b-ENP10-6	20	0,0183	0,0907	$4,0x10^{-3}$
PPy-b-ENP10-7	50	0,0085	0,0257	$2,8x10^{-3}$

[Py]: 0,237 mol/L [ENP10]:0,0154 mol/L T:25 ˚C t:24 h

The effect of concentration on the conductivity was examined for different concentration of CAN of Polypyrrole and ENP10 copolymer. The concentration of Ce salt varied between 0,064 mol/L and 0,0085 mol/L keeping the other parameters of polymerization constant. An increase in the ceric ion concentration caused the

polymerization yield to increase. The limiting conversation reached a maximum value when ceric ion concentration was 0,0470 mol/L can be shown in Figure 4.20. Increasing the Ce^{+4} concentration above this value resulted in the yield of polymerization to become inversely proportional to Ce^{+4} concentration, probably because of linear termination by Ce^{+4}. Besides, increasing Ce^{+4} concentration is known to cause a significant increase in the rate of oxidative termination of primary radicals compared with the rate of initiation. Oxidative chain termination and linear termination by Ce^{+4} ions probably was significant at higher Ce^{+4} concentration (0,0470 mol/L) conductivity became inversely proportional to the Ce^{+4} concentration. We see that the conductvities of these copolymers are not high enough,if it is compared with polypyrrole. The water-soluble of nonylphenolethoxylates diminishes the conductivity of copolymer becaue of its surfactant structure.

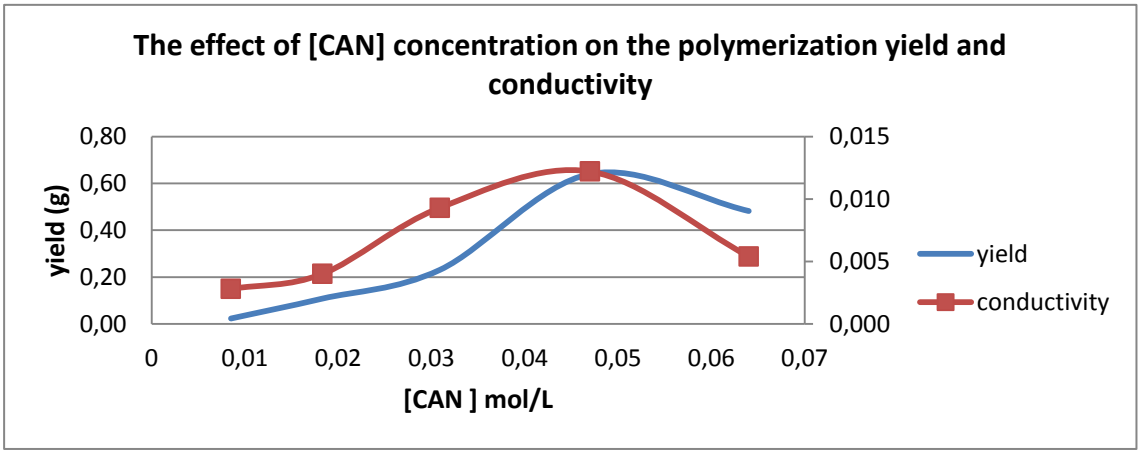


Figure 4.20 : The effect of [CAN] concentration on the polymerization yield and conductivity. [Py]: 0,237 mol/L [ENP10]:0,0154 mol/L.

Figure 4.21 shows the FTIR spectra of PPy-b-ENP10 copolymer The peaks at 780 cm^{-1}, 940 cm^{-1} are attributed to C–H wag- ging attributed to C–H wagging, peak at 1042 cm^{-1} indicative of =C H in plane deformation vibration, peak at 1101 cm^{-1} attributed to C-H in and out of plane deformations. The peak at 1208 cm^{-1} attributed to N–C stretching band . The characteristic peaks at 1560 cm^{-1} and 1462 cm^{-1} correspond to the C=C stretching, whereas peak at 1677 cm^{-1} C=N and C–N bonds . The occurrence of small peaks at 3253 cm^{-1} is assigned to presence of N–H stretching vibrations. The peak at 1384 cm^{-1} was due to a NO_3^- ligand incorporated into the polymer. This peak was always observed as a sharp band in the spectrum of

the copolymer. For ENP10 the spectrum with peaks etoksi (CH_3CH_2-O-) C-H stretching at 2909 cm^{-1} and C-O stretching peaks at 1185 cm^{-1}.

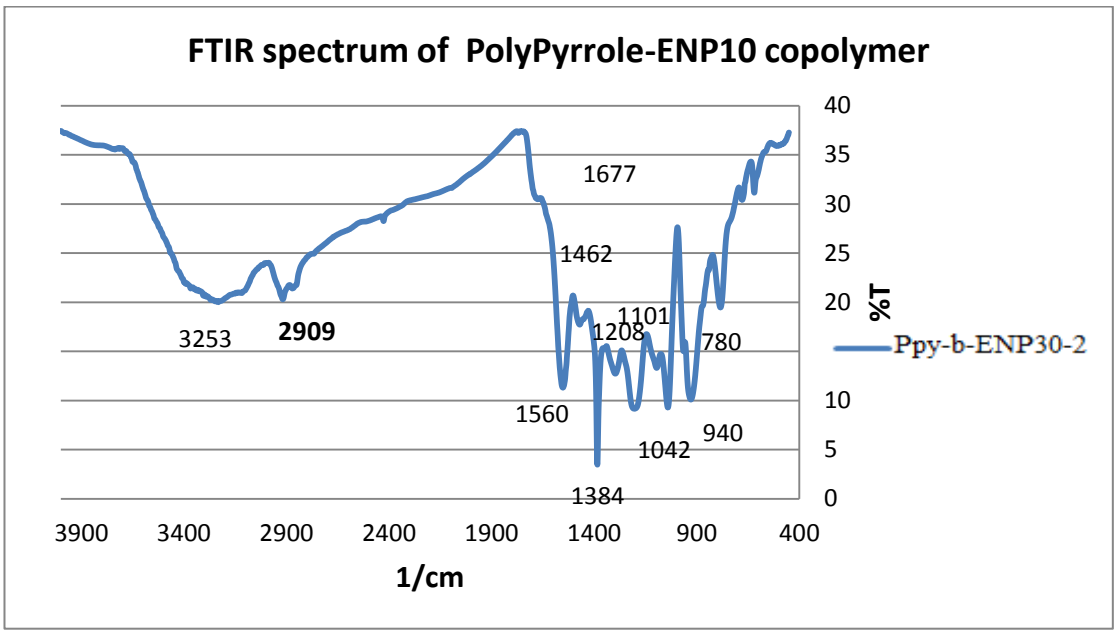


Figure 4.21 : FTIR spectrum of PolyPyrrole and ENP10 Copolymer(Ppy-b-NPE30-2)

The scanning elecron microscope sample pictures shows us that we obtain nano scale PolyPyrrole and ENP30 Copolymer particles can be seen in Figure 4.22.

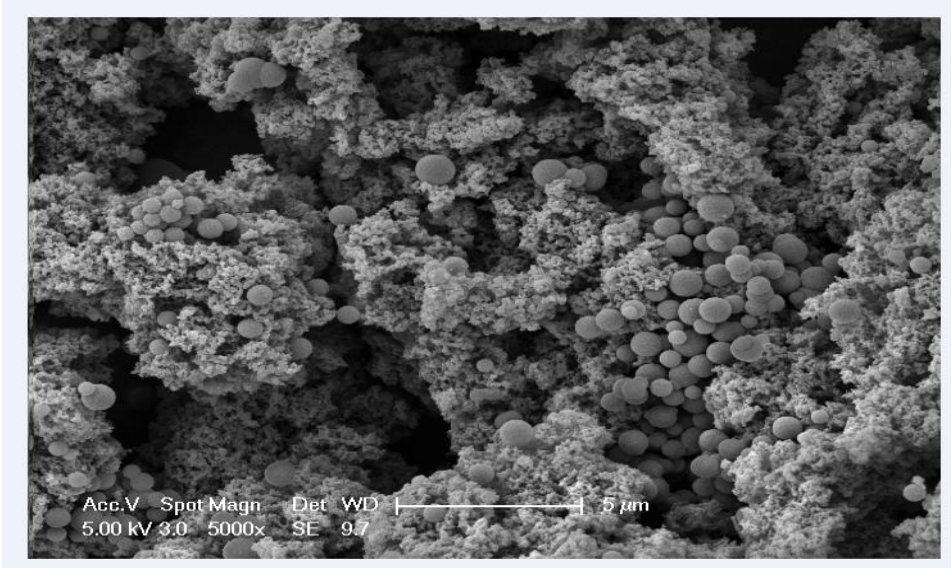


Figure 4.22 : The SEM picture of PolyPyrrole-ENP10 Copolymer PPy-b-ENP10-2 in 5µm

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5. CONCLUSION

The effect of concentratio on the conductivity was examined for different concentration of CAN. It is seen that , the conductivities increases with respect to the CAN concentration, of cource this result is expectable**.** It can be made such a commentary that increase in CAN concentration leads to emerge short polymer chains which are not satisfactory conductive but soluble. We can understand that CAN concentration directly effect the solubility and conductivity. An increase in the ceric ion concentration caused the polymerization yield to increase. Increasing Ce^{+4} concentration is known to cause a significant increase in the rate of oxidative termination of primary radicals compared with the rate of initiation. The result of oxidative chain termination and linear termination by Ce^{+4} ions conductivity became inversely proportional to the Ce^{+4} concentration.

Etoxylated nonly phenols-ceric ammonium nitrate redox pairs are effective initiators for aqueous polymerization of Polypyrrole at ambiant temperature to produce polymers with etoxylated nonly phenol chain ends, respectively. Soluble polymers with a conductivity 10^{-3} S/cm were produced. As we seen the serial experiments for polymerization yield seemed not to depend on the type of ethoxylated nonyl phenol.

These soluble and conductive copolymers may overcome difficulties in the applications of PPy homopolymers and open new application areas. Therefore, the copolymers may find a number of new application areas as well as existing PPy applications. Besides these PPy may uses in other areas because of their biodegredable non-ionic surfactant chain ends

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